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ASSAYING AND
METALLURGICAL ANALYSIS

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METALLURGY

AN ELEMENTARY TEXT-BOOK

By E. L. RHEAD

*Lecturer on Metallurgy, Municipal School of
Technology, Manchester.*

LONGMANS, GREEN, AND CO.
LONDON, NEW YORK, AND BOMBAY

ASSAYING
AND
METALLURGICAL
ANALYSIS

*FOR THE USE OF STUDENTS, CHEMISTS,
AND ASSAYERS*

BY

E. L. RHEAD

LECTURER ON METALLURGY, MUNICIPAL SCHOOL OF TECHNOLOGY, MANCHESTER

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LONGMANS, GREEN, AND CO.

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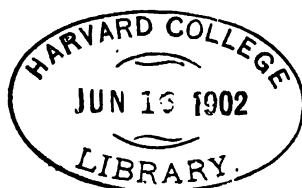
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P R E F A C E

THE object which the authors had in view in writing the present work was to provide the Student, Chemist, or Assayer with a handbook sufficiently comprehensive to include the greater part of the work likely to be required in the Laboratory or Assay Office. Most of the approved modern methods in general use are included ; but it would be impossible, even if advisable, to include all the variations which have been suggested by competent workers.

The directions for work and the descriptions of processes have been made as concise as possible, to reduce the size of the book ; but by the inclusion of the chemical reactions of the metals it has been sought to make the reasons for the procedure clear, and where it was thought necessary, chemical explanations have been given at greater length. Care has been taken to make the methods of calculation clear, using for the most part the approximations of the atomic weights commonly employed. In a few instances directions are given for conducting experiments to ascertain the kind of treatment suitable for a given ore, and the examination of work's products and solutions has also been described.

Part I. is devoted to laboratory appliances and general processes, useful hints rather than full descriptions being given.

In Part II. the general plan followed has been to consider under the name of each metal (1) the materials and products in which its estimation is commonly required, giving a brief description of their characters so as to make their identification easy ; (2) the dry tests for, and important chemical reactions of the metal, with, in some cases, special instructions for the detection of small quantities ; (3) the methods of conducting the dry assay by fusion or otherwise, followed by applications to special materials where modifications are necessary ;

(4) methods of dissolving substances and preparing solutions for the determination of the metal; (5) methods for the gravimetric, volumetric, and colorimetric determination, with the precautions necessary.

In Part III.—metallurgical analysis—an attempt has been made to group the very various substances to be dealt with in a compact manner, and, by cross-references inserted in the text, to, as far as possible, avoid repetition. The use of all specially marked measuring apparatus has been avoided, and the preparation of standard and other solutions required for a particular assay has been incorporated with the description of the method.

Many works have been consulted, including treatises on assaying and analysis by Mitchell, Blair, Furman, Ricketts, Kerl, Arnold, Beringer, Bailey, Brown, Crookes, and the engineering and chemical journals, and the authors gratefully acknowledge the assistance they have derived from those sources.

The thanks of the authors are due to Mr. J. G. Galletly, assistant to one of them, for the help he has given in reading the proofs.

In the Appendices a systematic method of keeping laboratory books has been included.

E. L. R.

A. H. S.

MANCHESTER, { *January, 1902.*
GLASGOW, }

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PART I.

ERRATA. •

Page 140, line 12 from bottom. *for* "red lead or litharge" *read* "litharge."

" " " 9 " *for* "lampblack" *read* "charcoal."

" 355. " 21 " *for* "Willans's" *read* "Williams's."

ASSAYING

AND

METALLURGICAL ANALYSIS

MODES OF ASSAYING.

Vanning Assay.—The metal or its ore is separated from the gangue by washing with water.

Dry Assay.—The metal is separated in a more or less pure state, by fusion with reagents to reduce the metallic compound and effect the removal of the associated substances in a liquid form in the slag. This is generally a rapid method, but the rapidity is often secured at the expense of accuracy, and has given way in many cases to wet methods.

Wet Assay.—The substance to be assayed is treated so as to obtain the metal it contains in solution as a salt. This solution may be treated for the removal of other substances which would interfere with the carrying out of the process and the metal estimated :—

(a) *Gravimetrically.* The metal or some compound of fixed and known composition is precipitated, collected, and weighed. From the weight of the precipitate the quantity of metal it contains is calculated.

The precipitation may be effected—

1. By displacement with another metal.
2. By the addition of reagents which produce an insoluble compound of the metal of definite composition.
3. Electrolytically.

(b) *Volumetrically.* The quantity of the metal present is determined by measuring the volume of a solution of a reagent, required to produce a known and definite reaction. The end of the reaction may be self-evident, or use may be made of an indicator which gives evidence of the presence of the slightest excess of the reagent. The strength of the solution employed is first carefully determined, by ascertaining its effect on solutions containing a weighed quantity of the pure metal or of a pure salt. By this means the test solution is “standardized,” and is termed a Standard Solution. The quantity to which each cubic centimetre of the solution is equivalent is marked on the stock bottle

B

and from the volume used for the assay, the amount of the metal in the assay solution is easily calculated. In many cases the standard solutions change so rapidly that they must be standardized before each set of determinations.

(c) *Colourmetrically.* Advantage is taken of some compound of the metal possessing a deep and definite tint. The amount of the metal is determined by the depth of the tint it produces in a solution of known volume, compared with the quantity of the metal required to produce the same depth of colour, under the same conditions of temperature, depth of liquid, etc.

In some cases a combination of dry and wet methods is employed, as in gold assaying. Where this is adopted, the concentration of the metal is more readily effected in the dry way.

SAMPLING.

NOTHING is more important to the successful assay of any material than the obtaining of a portion which shall represent the true character of the bulk. To effect this, very careful sampling is necessary. No attempt should be made at selection, but the removal of the portion should be carried out on some set plan.

In sampling material in bulk various methods are followed.

Sampling Machines.—Various arrangements are employed to—

(a) Divide a falling stream of material into two unequal parts, the smaller portion (sample) being diverted into a special bin.

(b) By means of a moving jaw or other device to divert the whole stream for an aliquot portion of the time occupied in the fall of the material at regular intervals.

The Bridgman Ore sampling machine "B" (Fig. 1) consists of three receptacles, revolving at different speeds. The upper receptacle separates a portion varying from $\frac{1}{8}$ to $\frac{1}{2}$ of the whole. This is quartered by the lower receptacle, which revolves at three times the speed of the upper in an opposite direction; and the sample it separates is in turn quartered by the lowest of the moving chambers, revolving three times as quickly and in the reverse direction. The average capacity of the machine shown is 2 to 4 tons per hour. It stands 36 inches high and covers a floor space of 18 inches square.*

In dealing with large quantities an automatic sampler of this nature is indispensable for accurate work. The sample obtained may represent from 2 % to 5 % of the total weight. Such machines are usually arranged, in large works, to give continuous samples, all the material passing through the sampler.

The sample thus obtained is then thoroughly mixed, crushed, or ground, if the pieces are of unequal size or character, and resampled. The operation is repeated until a sample a few pounds in weight is obtained, which is sent into the laboratory.

Hand Sampling.—This is done in a variety of ways. The broken material may be moved with spades by hand, every third, fifth, or

* Am. I. of M. E., Oct. 1891.

4 *ASSAYING AND METALLURGICAL ANALYSIS.*

seventh spadeful being thrown aside to the sample heap. If lying in a long narrow heap, a tolerable sample may be obtained by taking

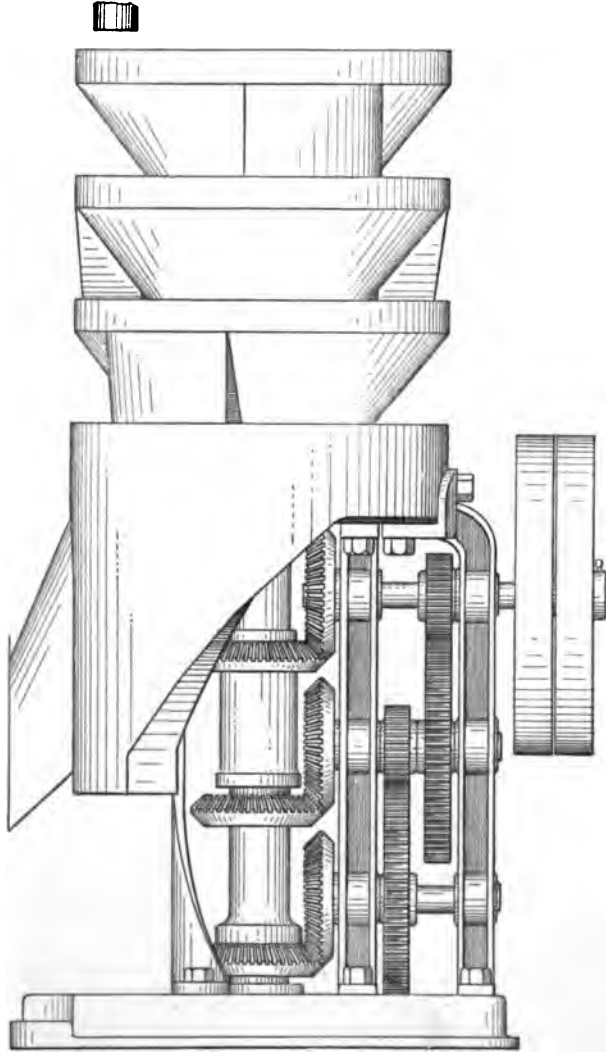


FIG. 1.

spades full alternately at the top and bottom of the pile, at short intervals on both sides, or better, by cutting trenches through the heap, taking

samples from the sides of the trenches, and reducing the material removed by quartering (see below). Methods of sampling large quantities by hand are not so reliable as mechanical treatment, but usually no other method is possible.

Sampling of Small Lots.—The sampling of small lots may be effected either by a machine or by hand. In the method of quartering the sample must first be broken and made into a conical heap, by throwing each shovelful on the top of the cone. The top of the pile is flattened by passing the shovel round the heap in spiral fashion till it is not more than 10 or 12 inches high. This heap is then divided into quarters. Two opposite quarters are removed, and the two remaining ones thoroughly mixed and again dealt with in the same way. This is repeated until the sample is small enough. Unless fine, the material should be broken or crushed between each quartering. Samples of 200 lbs. and under should not contain pieces larger than a bean, 50 lbs. than peas, and below 5 lbs. should be crushed to pass through a 13 to 20 sieve. The division of the final sample for sending out may be done in a similar manner or by means of a laboratory divider.

A metal sampler (Fig. 2), consisting of a series of troughs fastened together by strips soldered across their ends and arranged so that the spaces are the same width as the troughs, is very handy for sampling small lots of fine stuff. A shovelful of the material is shaken over the sampler, which is held at right angles to the falling ore stream, and retains a half of that which drops upon it. By moving it regularly from side to side a fair sample may be obtained, and by repetition the bulk reduced to reasonable size. The "split shovelling" of larger quantities is effected in a similar manner, the material falling from a chute.

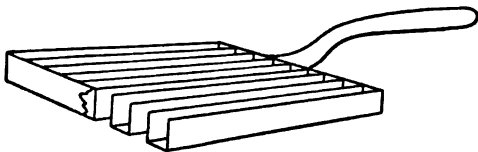


FIG. 2.

The Bridgman Sampler "C" is shown in Fig. 3. It is a modification of the larger Bridgman sampling machine. It is used for the quick and certain cutting down of the miscellaneous small samples (from 5 lbs. to 500 lbs. in weight) that are constantly being received in most assay offices. It will sample anything from fine pulp to crushed material of $\frac{1}{2}$ -inch or more in size.

The material is fed either by hand or (with large lots) from a suitably supported bucket, into the funnel, the divider being first set in rotation by hand, clockwork, or any other convenient power. The divider gives, as will be seen by inspection of the drawing, eight cuts to the

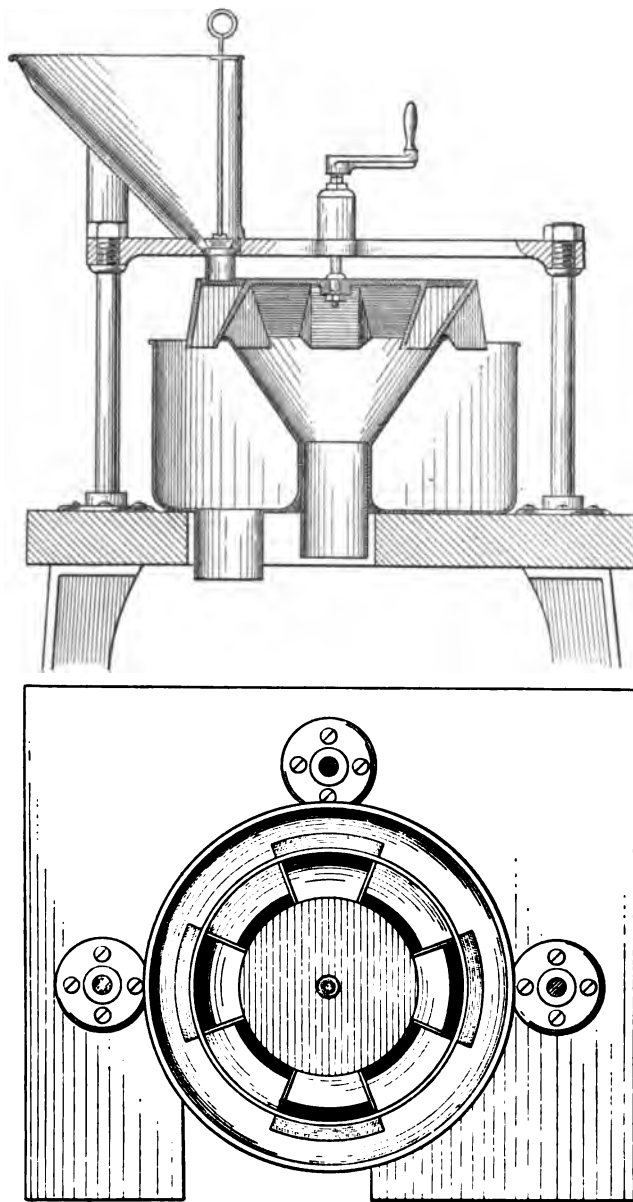


FIG. 3.

revolution, four being delivered to the funnel and four to the outer receptacle; that is, with uniform flow and speed, it cuts the material in half. The divider may easily run 100 revolutions per minute, giving in that time 800 cuts, a very much greater distribution and division than can be secured in any other way. The rejected sample passes down the dividing funnel, the retained portion into the surrounding chamber, from which it can be removed. The retained portion, should it be too large, may be cut again and again, until of suitable size. The operation is very accurate and very rapid, being about as fast as the material will flow through a one-inch spout.

Clarkson's Laboratory Divider, with one of the receiving cans, is shown in sectional elevation in Fig. 4. The hopper and dividing cone are carried by the central spindle, S, running in its bearing in the centre column, P, which supports the whole. The hopper itself is carried by six arms, A, three at the top and three at the bottom, one of each of which is shown. The material is placed in the hopper, H, which is then gently revolved so that the sample is discharged on to the divider, D, in a hollow rotating cylinder. The divider is circular, and is cut up into six equal segments by A-shaped partitions, which cut up the rotating tube of material, so to speak, into six separate and similar samples, which are discharged at O O into the receivers, of which C is one.

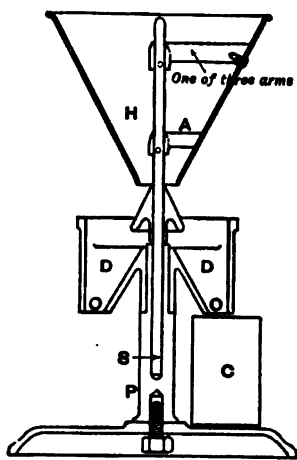


FIG. 4.

Sampling Metallic Products.—If solid, portions are chipped, sawn, or drilled from the mass.

Where possible, drilling should be resorted to. A half-inch drill (power-driven, if possible) is suitable for the purpose. It should be run through the metal, and not merely part of the way through. Holes should be bored through the ends and middle of a number of bars selected in regular order, every third, fifth, or seventh being taken.

In dealing with small ingots one hole is sufficient. The drillings must be clipped or broken down and sampled for analysis, taking care that the dust is sampled with the larger stuff.

Soft metals, such as lead bullion, which are undrillable, should be chipped out, on top and bottom of the ingots at each end, the same amount being taken from each part. Or better, the ingot may be sawn through at the middle and ends, the sawings being taken as the

sample. If the samples taken are too large, they may be melted together under charcoal at as low a temperature as possible and the resulting ingot sampled to the desired extent.

Some metallic substances are too hard to be drilled or chipped satisfactorily. In that case, portions taken with as much regularity as possible must be crushed down on a hard plate, or in the steel mortar, and sampled. If the material is liable to great variations, a large sample must be taken, crushed, mixed, and sampled down to convenient bulk.

Sampling Molten Materials.—This is best accomplished by means of a stout wrought-iron spoon, with a long handle. A convenient size is 3 inches long by $\frac{1}{2}$ inch wide, and $1\frac{1}{2}$ inch deep. The sample may be taken from the bath of metal in the furnace, or in the case of cupolas, held in the stream of metal, slag, matte, etc., as it flows from the furnaces. In sampling from the bath, unless the metal is boiling and thus kept well mixed, the sample should be taken after vigorous rabbling. With such metals as have any tendency to separate in layers of varying composition, *e.g.* cast iron, two samples at least must be taken, one at the beginning, and the other at the end of the cast. These must be broken up, thoroughly mixed and sampled, to give the average composition of the cupola metal.

DETERMINATION OF MOISTURE IN ORES AND PRODUCTS.

THE determination of the moisture is of the utmost importance in buying material. The sample should be taken independently from the bulk, where possible, just before, or at the time of weighing, and sealed in a bottle. If a corked bottle be used the cork should be soaked in paraffin, if a stoppered bottle then paraffin should be melted round the stopper. When the determination is to be made on the spot, the samples may be placed in open tins or other vessels and placed under a cover with a vessel of water (unless hygroscopic), as much care as possible being taken not to place them where the temperature differs from that of the ore mass. In cases where the material requires crushing during sampling the moisture sample may be taken from the assay sample.

(a) The moisture present may be determined by heating a weighed portion on a watch glass in a water bath till the weight is constant. The loss is moisture. In dealing with hygroscopic bodies the watch glass should be covered, and the weighing done in an atmosphere dried by calcium chloride. In dealing with some bodies, *e.g.* coal, prolonged exposure to a temperature of 100° gives erroneous results. In such cases the time of heating is limited to one hour.

(b) Another method consists of taking a weighed quantity of the substance in a porcelain boat, placing it in a wide glass tube, fitted at each end with a cork and exit tube. One end is connected with tubes containing calcium chloride and pumice soaked in strong sulphuric acid, to dry the air drawn over the sample by an aspirator, and the other with a weighed calcium chloride tube, to which is attached a second calcium chloride tube, to prevent moisture from the aspirator attached to it passing into the weighed tube.

Where a low temperature only is admissible the dry air is warmed by passing through a bent tube, heated in a water bath or beaker. If higher temperatures are admissible the tube containing the boat may itself be heated. The increase in weight of the calcium chloride tube gives the moisture in the sample. This tube should be provided with

indiarubber caps, stopped with bits of glass rod, which are put on while weighing and before use.

(c) The usual method of determining moisture commercially is to take from 200 to 400 grms. ($\frac{1}{2}$ to 1 lb. 1 oz. = 28 grms. approximately), and dry it in an enamelled pan over a bunsen provided with a rose, or over an open assay furnace, with constant stirring at a temperature from 100°–120° C. (212°–248° Fahr.) till, when made into a heap and hollowed a little, a plate of thick glass rested upon it is not dimmed by steam. Great care must be taken with oxidizable bodies, such as copper precipitate, that the temperature does not much exceed 212° Fahr., or actual gain in weight may occur from oxidation, even though the sample contains moisture. Small samples may be dried over a bunsen in a weighed platinum or porcelain dish.

FURNACES.

Wind Furnaces.—These are employed for heating crucibles and may be of any required size. For laboratory purposes, experimental work, it is essential that the draught arrangements should be under perfect control.

Figs. 5 and 6 show a suitable form of furnace. The flue is provided with a damper, and the ashpit is closed, air being only admitted to the fire by a sliding door, D. The stoppers, SS, above the level of the fire-bars, are only provided for cleaning purposes, and removing clinker—a considerable advantage when the furnace

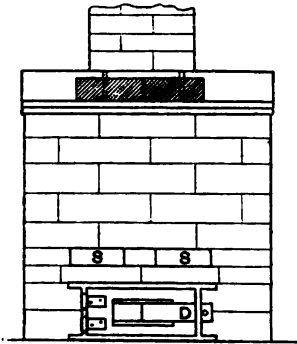


FIG. 5.

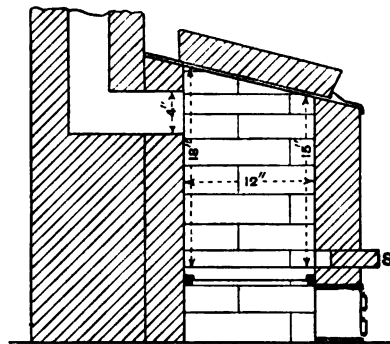


FIG. 6.

is in use for long periods. The top is sloping, and the cover of firebrick blocks is divided, so as to allow inspection of the interior. The dimensions of the principal parts are shown in the drawings. If a larger furnace than that shown is required, great care should be exercised in providing a flue of the necessary size. The main flue should have a sectional area not less than $\frac{1}{3}$ that of the sum of the grate areas of all the furnaces leading into it, and be provided with a damper. A stack 30 to 40 feet high will then be sufficient, and if higher a less area will suffice. The space in front of the furnaces should be flagged or covered with concrete. This furnace is designed for burning coke. For charcoal the chamber should take the form of an inverted

truncated pyramid. For general assaying purposes, a 9 or 12 inch furnace is satisfactory. Large furnaces (over 14 inches) should be built below the floor-level.

Manipulation of Furnace.—Much will have to be learnt by practice, but the following hints will be useful. When a low temperature is required the furnace should be lighted in the usual way, and when fairly alight the ashpit damper closed and the flue damper nearly shut. More broken coke, as may be necessary, should then be added, and, with a long poker, well mixed with the fire. Make a hole for the reception of the crucible and put in an old pot, to be afterwards replaced by that containing the assay.

NOTE.—The crucible should be placed so that the fire comes quite to the top and slopes upward to the sides of the furnace. This causes the line of least resistance to the draught to be up the sides of the crucible which consequently gets the benefit of the heat. If the fuel slopes downward, the gaseous current passes up nearest the furnace walls and heats them rather than the crucible.

When the fuel has been added and mixed up, the furnace should be closed and the heat allowed to diffuse uniformly, and, if necessary, a little more air admitted. Then remove the old pot and put the assay in its place. It must be borne in mind that once an enclosed furnace, such as is here employed, is fairly heated, it loses heat but slowly, and consequently very little combustion of the fuel is required to maintain the temperature when once it has been attained.

If the furnace fire is already too hot and the closing of the dampers will not cool it sufficiently, it is well to drench the coke, to be added to the fire, with water after breaking, before mixing with the fire already in the furnace. In some cases part of the fire may be drawn through the opening S.

The same method of stoking is also applicable for high temperatures, with, of course, greater freedom of air supply.

In order to heat crucibles most intensely they should be placed so that the bottom is only some 3 to 4 inches above the fire-bars, and if they are to remain in for long periods a stand or piece of fire-brick, resting on the fire-bars should be provided to prevent the pot sinking to the bars as the fire burns away, and from upsetting. It should be borne in mind that, in a furnace such as the one under consideration, the cold air entering the fire absorbs a considerable quantity of heat by its expansion, so that the zone of highest temperature is a little above the fire-bars. The higher parts of the fire are only heated by convection, the upper layers of fuel abstracting the heat from the ascending current of hot gases. The exact height of the zone of active combustion depends on the rapidity of the

air current (regulated by damper) and the nature and disposition of the fuel.

The coke for furnaces of the dimensions here described should be broken to the size of macadam, free from dust, and should be carefully packed round the crucibles.

A little care exercised in the management of a furnace will be well repaid in fewer disappointing results, and saving of time.

A portable crucible furnace made by Morgan's, Battersea, is shown in Fig. 7. Gas crucible furnaces, in which arrangements of Bunsen burners are employed, are supplied by various makers—Griffins, London; Fletcher, Warrington; and others.

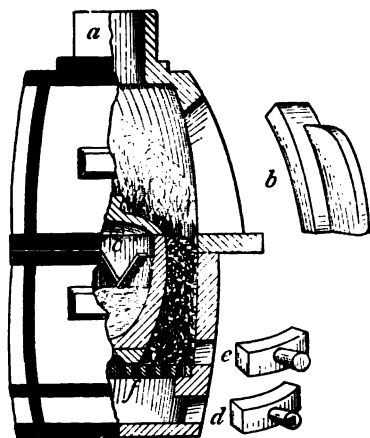



FIG. 7.

Muffle Furnaces.—The muffle itself is a -shaped clay vessel (M, Fig. 8), stopped or partially stopped at one end, and open at the other. This is heated in a fire-chamber, and the material to be heated

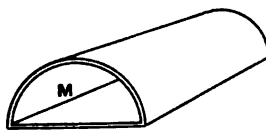


FIG. 8.

placed inside in crucibles, dishes, or cupels. Closed muffles are used when it is necessary to exclude the furnace gases and air from the material.

Perforated muffles are used when the admission of air for oxidating purposes is necessary. The draught induces a current of air through the chamber, which can be moderated by dampers, and by the door of the muffle. Various forms of muffle furnace are employed.

Figs. 9, 10 show a bullion furnace for assaying purposes, for burning coke. It is made of iron plates, lined with fire-brick slabs. The muffle is supported back and front, is $10\frac{1}{2}$ in. long, 7 wide, and 4 in. high. The muffle door is iron framed, and slides in guides, and is supported in position by the teeth of the rack, as shown. The fire-bars are $4\frac{1}{2}$ in. from the bottom of the muffle, the grate being 14 in. by 10 in. Above the grate level is a narrow door, 2 in. wide, for clearing the bars and arranging coke. The ashpit is provided with sliding doors for regulating draught. The firing door above the muffle is hinged at the bottom, and opens forward, forming a convenient rest for coking, and

preventing the coke falling down in front. This door has two latches, which catch in the racks on either side, so that it may be opened to any desired extent in regulating the draught. No damper is necessary.

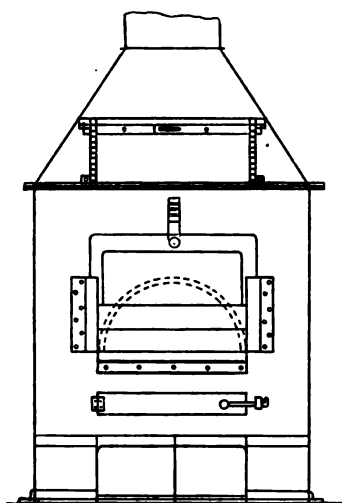


FIG. 9.

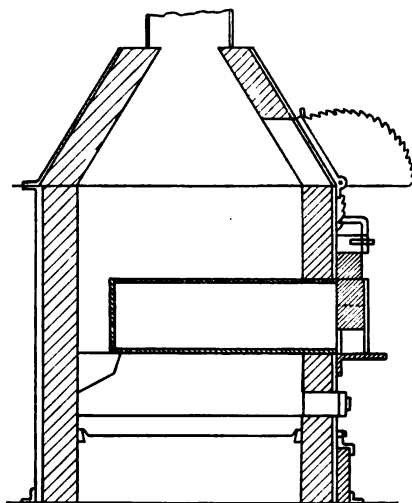


FIG. 10.

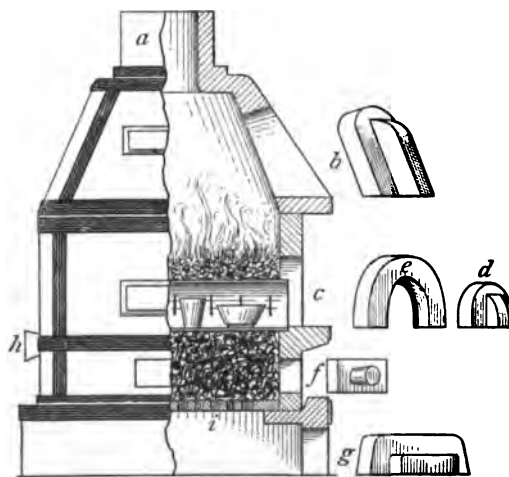


FIG. 11.

Fig. 11 shows a portable cupellation furnace of the Morgan Crucible Company, Battersea, for burning coke. It is made of three sections

fire-clay, bound with hoop-iron. The top section has a socket, *a*, for the reception of a sheet-iron stove-pipe connected to the chimney and the stoking door, *b*. The middle section contains the muffle opening, *c*, and an opening, *f*, in front. There is an opening similar to *f*, but smaller, on each side. The muffle rests on a ledge in front, and at the

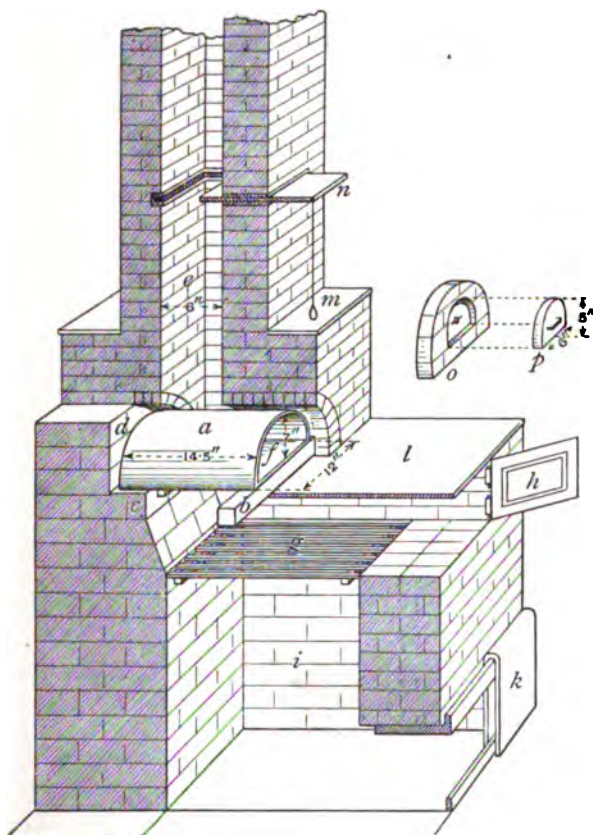


FIG. 12.

back, on a fire-clay wedge, *h*, which passes under the muffle *c*, is a fire-clay arch, and *d*, the muffle door. The bottom section forms the ashpit and the support for the fire-bars, *i*, which consist of a cast-iron grid cast in halves. *g* is the ashpit opening, and serves, as in Figs. 9 and 10, for regulating the draught.

Fig. 12 shows a muffle furnace for burning coal.

Description of Coal Muffle.—The muffle, *a*, is $14\frac{1}{2}$ in. long, 12 in. wide, and 7 in. high, and is set with a slight slope forward, being about an inch higher at the back. It rests upon the support, *b*, in front, and the forked support, *c*, at the back. It is contained in the arched chamber, *d*, between which and the top of the muffle is an interval of 2 in. *e* is the chimney flue, 6 in. square, provided with the damper, *n*, and handle, *m*. *g* is the fire-grate; the grate is 20 in. long, 10 in. wide, and 11 in. below the bottom of the muffle. *h* is the firing door, 8 in. high; *i*, the ashpit; and *k*, a sliding ashpit door, which also serves as a draught regulator; *o* is the brickwork stopping for the arch, *j*, in front of the muffle; and *p*, the muffle door, 6 in. long by 5 in. high.

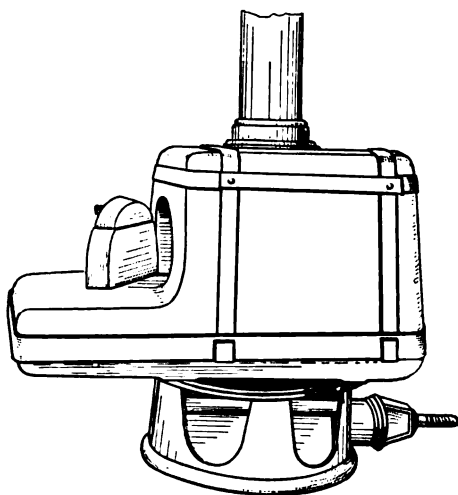


FIG. 13.

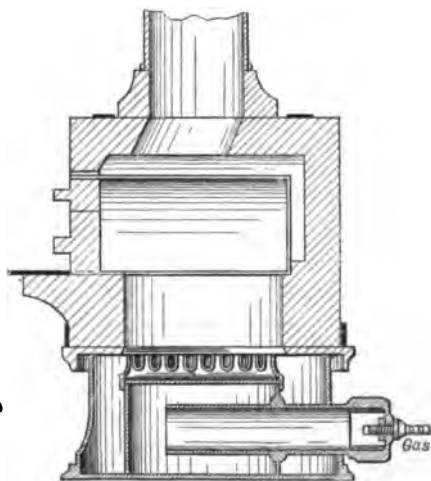


FIG. 14.

The temperature of the muffle may be regulated much in the same way as a wind furnace, by means of the ashpit and flue dampers, and the charging-door at the top, by opening which—when the flue damper is slightly open—further control may be obtained. In stoking, the fuel should be carefully pushed down beside the muffle, and drawn underneath it through the opening, *f* (Fig. 11).

Figs. 13, 14, 15 show gas muffle furnaces, made by Fletcher, Warrington, in which Bunsen burners supply the place of the fire, and are self-explanatory. Figs. 13 and 14 show the older and more generally used form. In lighting, remove the muffle and introduce a light; then turn on the gas, and regulate the temperature to suit the work in hand.

Oxidation processes such as calcining, roasting, scorification, and cupellation, are conducted in muffle furnaces. In cupellation and scorification the bottom of the muffle should be covered with bone ash. A gas muffle is very convenient for burning filters, ash estimations, and general analytical work.

A portable prospector's furnace, designed to meet, in a simple, durable, and portable form, all the requirements of the prospector, is shown in Fig. 16. It can be used for muffle or crucible work, and accommodates a muffle 12 in. \times 6 in. \times 4 in. and crucibles up to 40 lbs. capacity. The furnace consists of strong fire-clay slabs with rebated

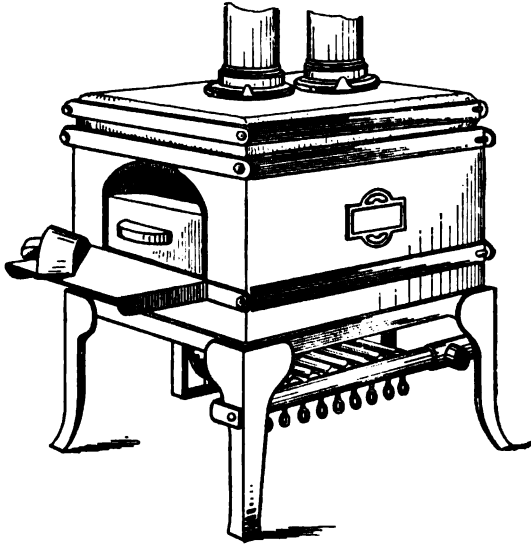


FIG. 16.

edges, ensuring tight joints, which are kept in position by the top plate being screwed down. The casing is of stout sheet-iron with removable fittings. For assaying, the muffle door, C, is provided with a mica sight-hole through which the contents of the muffle can be watched. The slab, K, is supported by the projecting ends of the fire-bars, and forms a convenient shelf on which to place the scorifiers, etc. The furnace can be used for crucibles by closing the muffle aperture with the clay stopper, N, and the contents of the crucible can be inspected from time to time through the sight-hole, A, thus obviating the necessity of removing the furnace cover. The total height of the furnace is 28 in.; depth, back to front, 14 in.; and width, 16 in.; diameter of chimney collar, 5 in. Total weight of furnace, complete, 130 lbs.

The "injector" furnace (Fig. 17) is a small gas furnace for heating crucibles. The casing is cylindrical, and the crucibles are inserted by

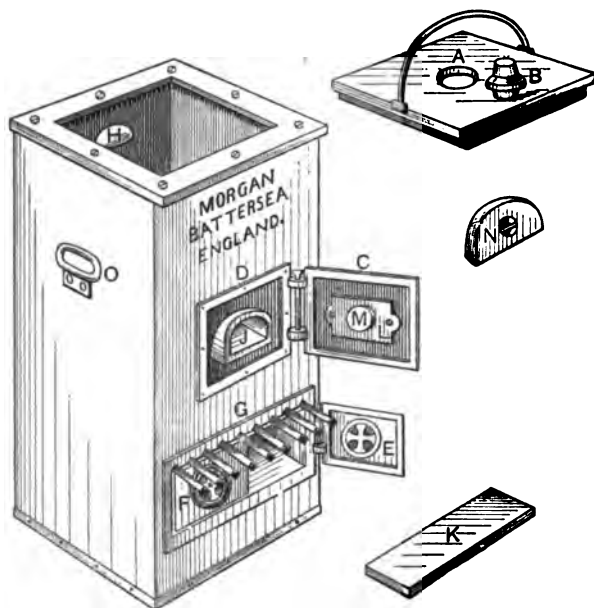


FIG. 16.—A, fire-clay cover; B, stopper for ditto; C, cast-iron muffle door; D, frame for ditto; E, F, cast-iron draught doors; G, frame for ditto; H, chimney collar; J, muffle (12 in. \times 6 in. \times 4 in.); K, fire-clay slab, to rest on projecting ends of fire-bars and form shelf; L, M, mica sight-hole and plate; N, plug for closing muffle aperture; O, lifting handles.

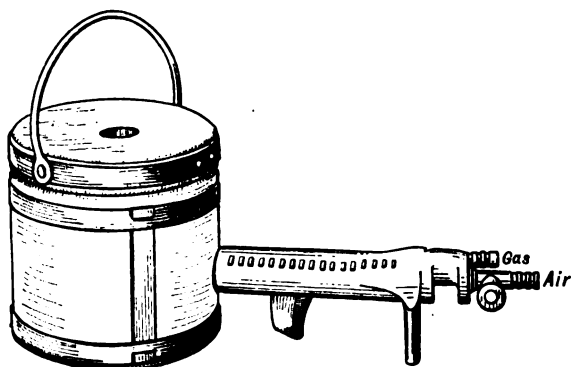


FIG. 17.

removing the lid. The blow-pipe enters at the side. A similar furnace designed to use compressed oxygen is also obtainable.

Furnace Tools and Laboratory Appliances.—

1. Tongs, stirring rods, etc., employed for various purposes are shown in Fig. 18.

- (a) Tongs for raising small crucibles and light general work. They are 24 inches long, of $\frac{1}{2}$ inch round iron, with heavier jaws. For heavier work the handles are straight.

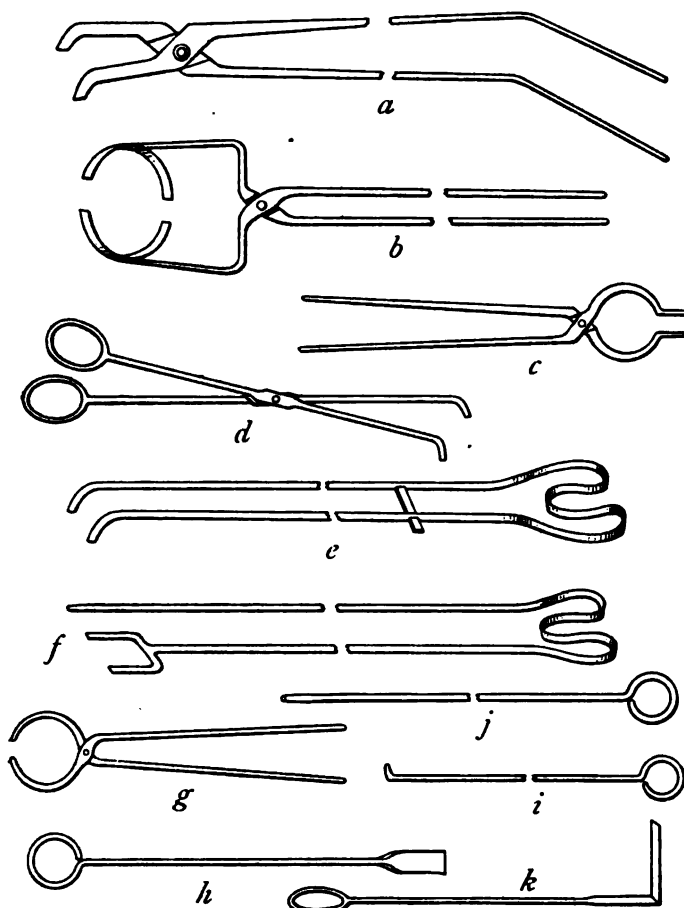


FIG. 18.

- (b) Basket-tongs for gripping larger crucibles.
 (c) Tongs for general purposes.
 (d) Very light tongs for lifting dishes, covers, etc.

- (e) Cupel tongs—light spring tongs, from 15 to 28 inches long, for handling cupels and fragile bodies.
- (f) Scorifier tongs. The fork is passed under the lower part of the scorifier, and the upper, single limb, is pressed over the top of the scorifier, so that its contents may be poured out.

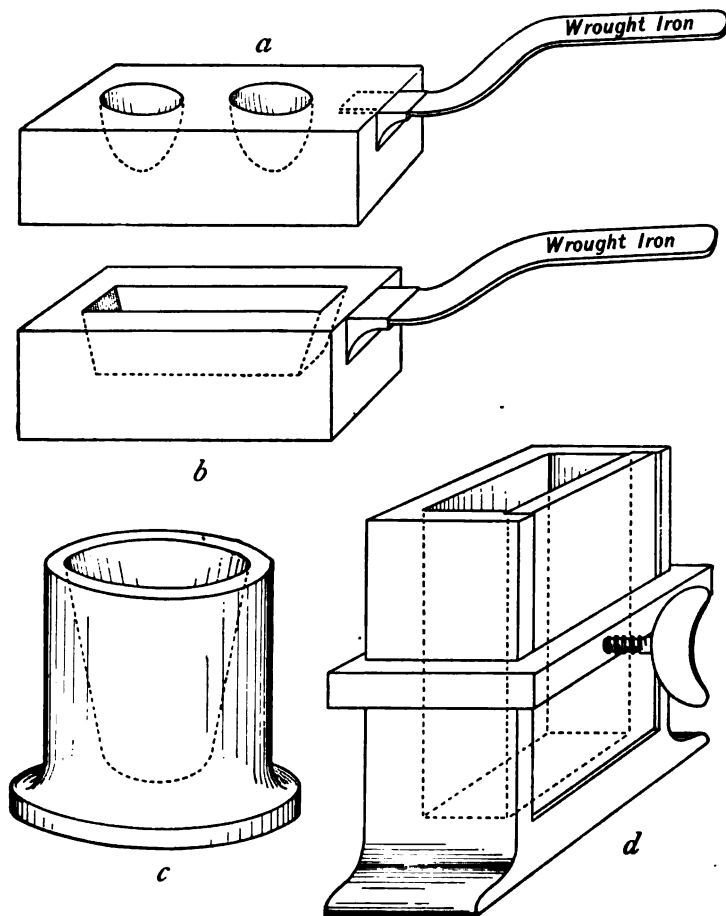


FIG. 19.

- (g) Bow tongs.
- (h) Straight stirring rod for stirring materials when roasting in crucibles in a wind furnace.
- (i) Bent stirring rod, for use in roasting and calcining operations conducted on dishes in a muffle.

- (j) Poker of $\frac{3}{4}$ -inch round iron for breaking up clinker on furnace bars and similar purposes.
- (k) Scraper for bottom of muffle, etc.
2. Ingot moulds, of various forms, for receiving the fused contents of crucibles or scorifiers, are shown in Fig. 19.
- (a) Button mould. The cavities are $1\frac{3}{4}$ inch diameter, and $\frac{7}{8}$ inch deep.

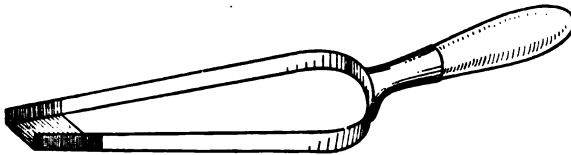


FIG. 20.

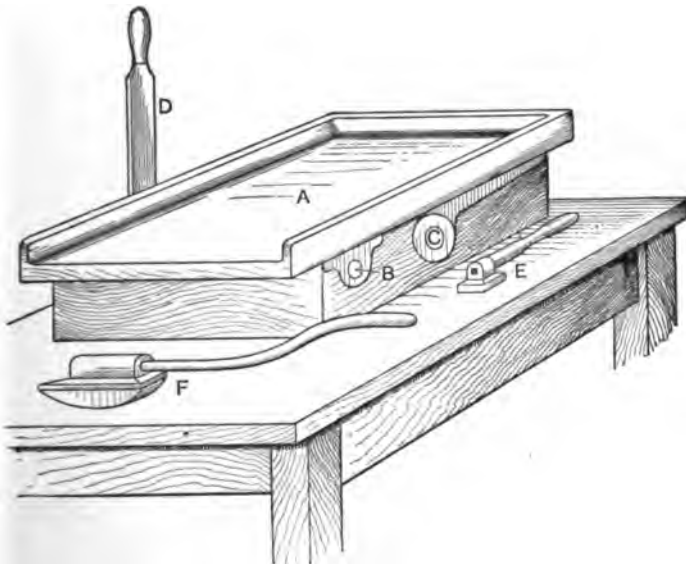


FIG. 21.

- (b) Flat ingot mould. The cavity is $4\frac{1}{2} \times 1\frac{1}{2} \times \frac{1}{2}$ inch.
- (c) Conical or flask mould. The sizes vary.
- (d) Mould for casting flat ingots for rolling.
3. Copper scoop, with wooden handle, for charging crucibles (Fig. 20).
4. Pulverizing appliances. Fig. 21 (A) shows a table for crushing samples.

- (a) The cast-iron plate, A, is 2 feet by 1 foot 6 inches, and 1 inch thick. The raised edge is 1 inch high. The plate is hinged at B. The axis, C, carries the lever, D, by which the plate is tilted to remove the powder; E is a crushing hammer; F is a bucking iron or muller 6 inches long, 4 inches wide, 1 inch thick at the end, and $1\frac{3}{4}$ inch or more in the middle. The curved face is rubbed to and fro over the surface of the plate with a rocking motion, the left hand pressing on the muller and the right hand grasping the handle. The faces of both plate and muller must be planed true and smooth.
- (b) Ring and plate used with hammer. The material is placed in the loose conical ring, A (Fig. 22), resting on the iron plate, B, and crushed by striking with the hammer, C.

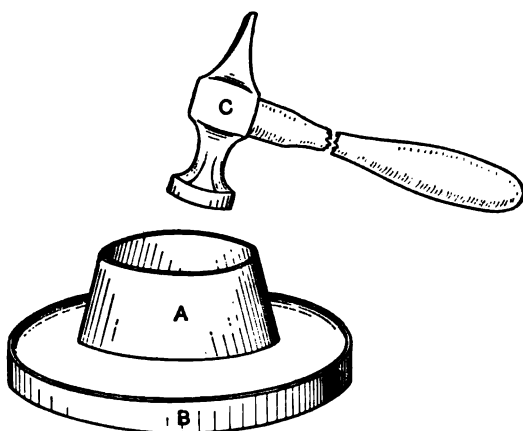


FIG. 22.

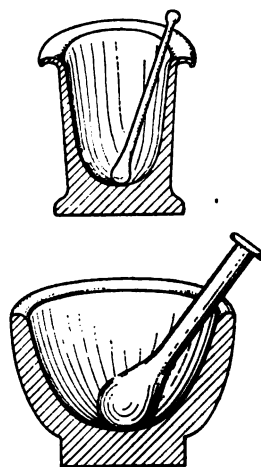


FIG. 23.

- (c) Iron mortars and pestles of shapes shown (Fig. 23) in various sizes.
5. The steel mortar (Fig. 24), is used for crushing hard materials. The substance is placed in the cylinder, A, resting in a socket in B. The plug, C, which fits A accurately, is put in and hammered. The faces of B and C are made as hard as possible.
- Porcelain and agate mortars are also required.
- A coffee mill (Fig. 25) is sometimes useful for grinding samples.
- Hare's feet for wiping out mortars.
6. Sieves, 30, 60, and 90 mesh, or 40, 60, and 80 meshes to the

linear inch, in nests with cover and receiver, as shown (Fig. 26). Simple open sieves are also used ; 18, 18, and 25 mesh being the most useful sizes.

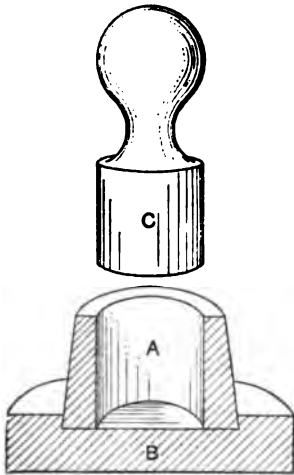


FIG. 24.

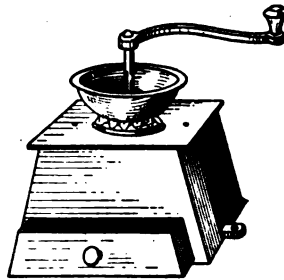


FIG. 25.

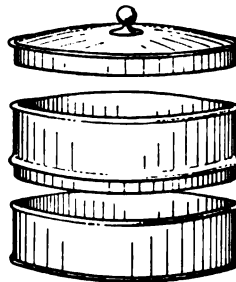
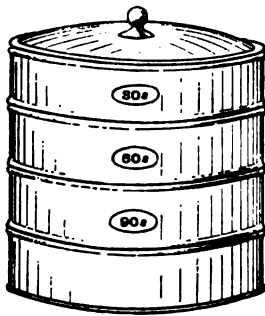


FIG. 26.

7. Crucibles and Covers. Clay, plumbago, and carbon crucibles of various sizes are used. The forms in more common use are represented in Fig. 27.

(a) Battersea round ; (b) triangular ; (c) Cornish copper assay ; (d) London round lead assay ; (e) fluxing pot ; (f) tin assay ; (g) skittle pot for fusing substances which are liable to boil up ; (h) iron assay with brasque lining. See Iron Assay.

In general, deep crucibles are preferable where very fluid slags are

produced, and the metal or other product has a high specific gravity. Shallower pots are employed where the slag is more viscous, or where oxidation effects are required as in roasting copper regulus, and in refining, etc.

Coarse-grained crucibles do not pour as clean as smooth ones, and are more liable to be acted on by fluxes. Hence fluxing pots, which are of exceedingly fine grain, are employed in particular operations. Great care is necessary in heating them, owing to the readiness with which they crack if rapidly heated. The resistance of a crucible to the action of fluxes may for all practical purposes be determined by heating

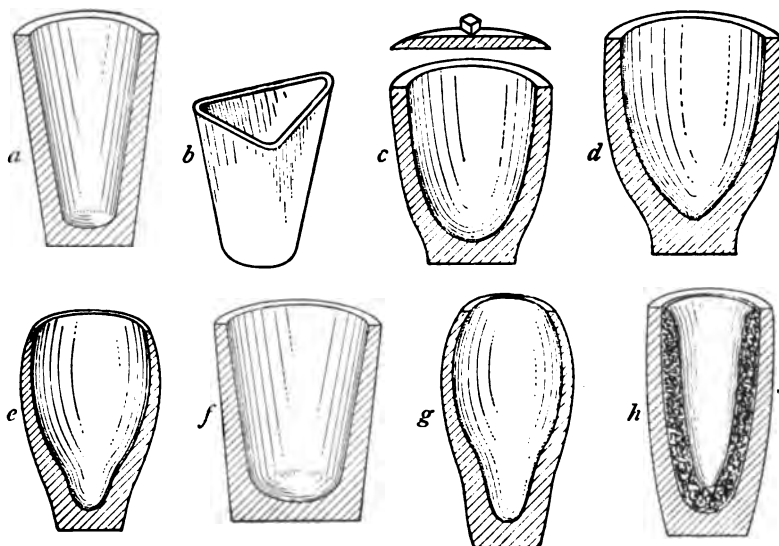


FIG 27.

litharge in it. The effects produced are compared with those produced on a crucible of known quality similarly treated. For melting metals, plumbago crucibles are employed, except in cases where the crucible is to be broken up after use. For small quantities crucibles of compressed carbon are to be preferred to any other kind. They contain no admixture of clay as do plumbago pots, and can be heated and cooled rapidly without danger. They are obtainable through Messrs. Woolley, of Manchester. Both graphite and carbon pots pour clean, owing to the smoothness of the sides.

Clay crucibles may be rendered impervious to liquids and gases by treatment with a wash of lime in borax water and heating.

Crucibles of malleable iron are sometimes employed in treating

sulphides, etc. See Lead Assay. They should not be heated above the melting-point of copper unless placed in a clay pot, on account of the rapid oxidation that occurs. Cast-iron pots are sometimes employed, and are much cheaper.

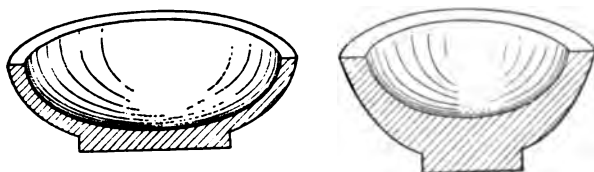


FIG. 28.

8. **Scorifiers and roasting-dishes** of clay of various sizes (Fig. 28). These are very smooth inside, and the former are made with thick sides and bottom, because the oxide of lead produced in scorifying fluxes the clay.

9. **Cupel mould** (see Fig. 29).*

Cupels *b* and *c* (Fig. 30). The latter is the French shape. *a* is a small clay annealing cup for gold assay.

10. **Mould for making small crucibles** (Fig. 31). The wood base, *B*, has a gunmetal ring, *c*, having slots at *b*, through which the lugs, *a*, on the gunmetal flask, *A*, pass, and by a partial turn pass under the ring and hold the flask firmly in place. *C* is a wood plug with a projecting spike, which enables it to be placed centrally in *A*. The spike fits into a hole in the middle of *B*. A gunmetal ring encircles *C* at the shoulder, containing a notch, *d*,

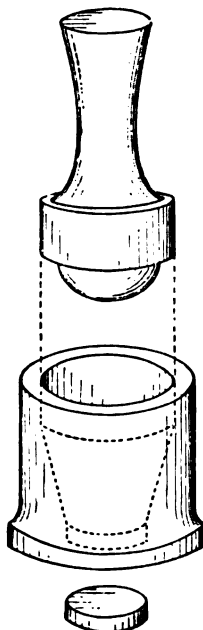


FIG. 29.

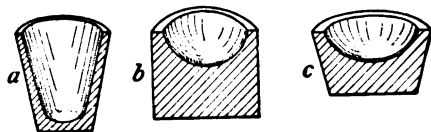
*Cupels*

FIG. 30.

the sharp edge of which serves as a cutter to remove surplus clay when twisted round in *A*. *D* is a plug which is used after *C*, a small pellet of clay having first been dropped in to stop the hole made by the spike. When in use, the various parts should be well oiled.

* For making cupels, see Silver Assay, p. 109.

11. A hammer, anvil, vice, steel chisel, mallet, files and rasps, stiff brushes, hand shears, and lens, are required for separating, testing, and examining products.

12. For mixing substances, a 6-inch steel spatula or palette knife and highly glazed paper are required.

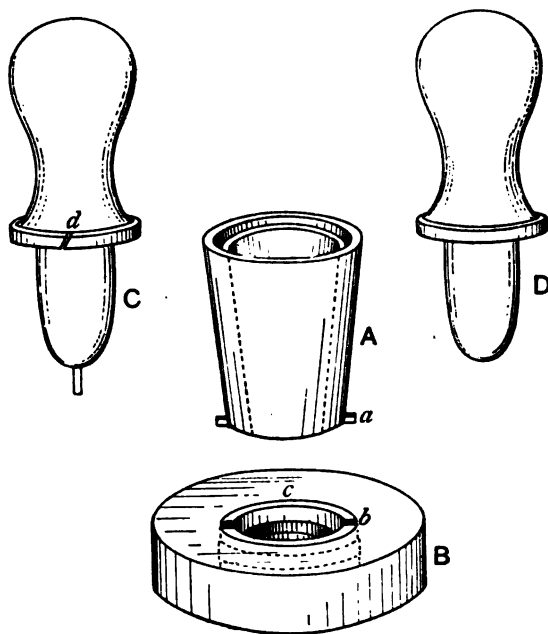


FIG. 31.

A jeweller's flattening mill (Fig. 32) with 2 or 3 inch steel rolls is required for rolling out metals. It should be kept with great care, and as bright as possible.

Metal shears (Fig. 33) are useful for cutting sheet metal.

A small hand-drill (Fig. 34) for sampling ingots, is necessary.

A large fume chamber will be required. This is even more essential than in a chemical laboratory, and should be larger. The hot plate (Fig. 35) should be enclosed, or put to front and side of the fume chamber. It consists of an iron plate about $\frac{3}{8}$ to $\frac{1}{2}$ inch thick, heated by a long Bunsen burner.

Preparation of Sample.—All materials for assay should be reduced to a very fine state of division, and sifted according to requirement. This ensures thorough admixture and, so far as

possible, uniformity of the sample. For methods of sampling, see p. 8.

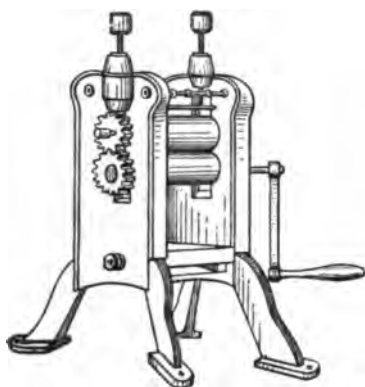


FIG. 32.

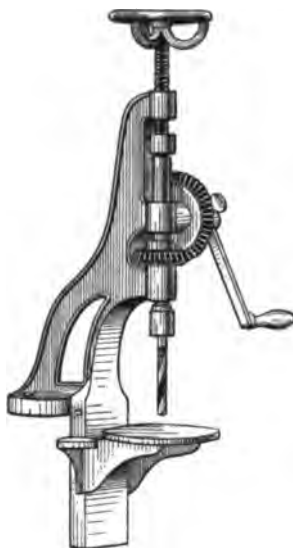


FIG. 34.



FIG. 33.

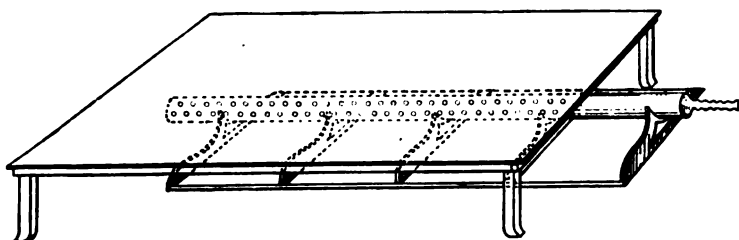


FIG. 35.

BALANCES AND WEIGHTS.

(1) A ROUGH pair of scales for weighing large samples of ore, fluxes, etc. Any ordinary scale will answer. That shown in Fig. 36 is a convenient form.

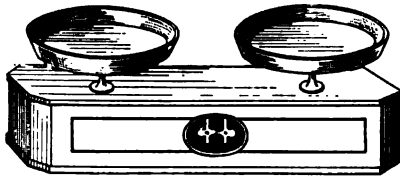


FIG. 36.

(2) A small balance (Fig. 37) for weighing ore for assay, fluxes, and large buttons. It should turn with about 3 to 4 milligrammes, *i.e.* about $\frac{1}{20}$ grain. It should have levelling-screws, movable pans, and a level.

(3) An accurate chemical balance (Fig. 38) turning easily with $\frac{1}{10}$ milligramme when loaded. This is used for all accurate weighings,

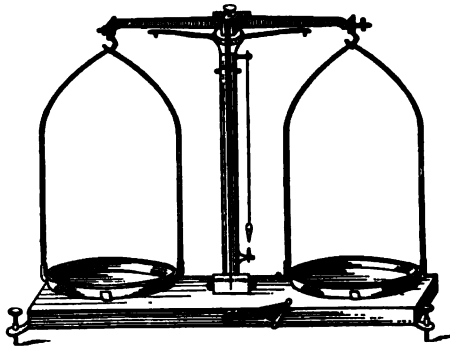


FIG. 37.

except gold and silver assay. The one shown is by Oertling, London. It has an 8-inch beam, and carries a load of 250 grammes.

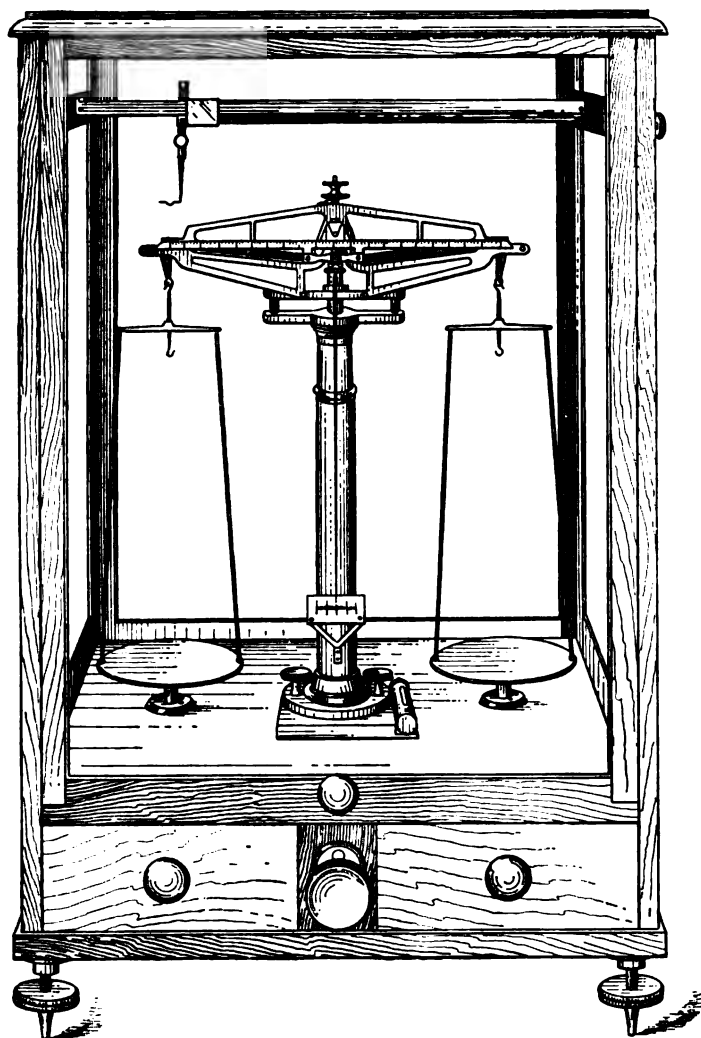


FIG. 38.

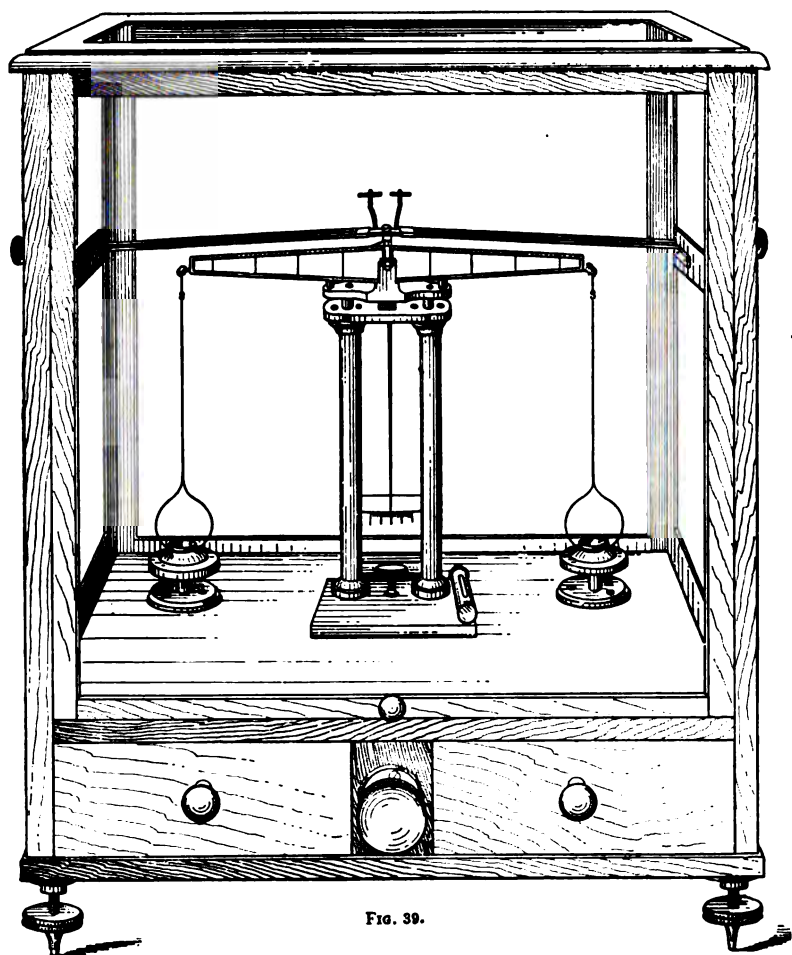


FIG. 39.

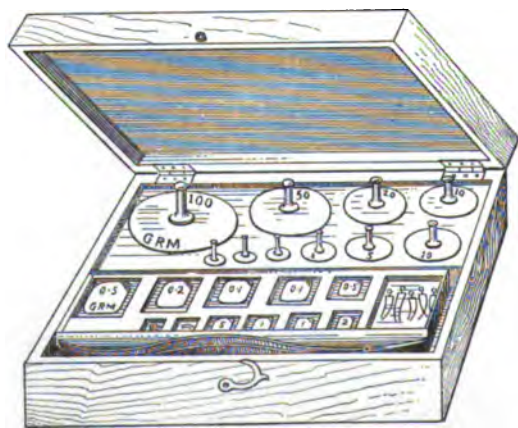


FIG. 40

(4) A bullion balance (Fig. 39) of the greatest accuracy and sensitiveness is employed to weigh assay prills of gold and silver. It is made as light as possible to ensure sensitiveness, and must be handled with the greatest care. The beam is divided on either side so as to read to 0.001 ($\frac{1}{1000}$) of a grain, or 0.02 milligramme, according to the weight of the rider used. It must be adjusted with the greatest care by dusting with a camel-hair brush, and levelled and tested before each set of weighings is made. See Weighing.

Of the weights employed, those used for weighing materials in bulk may be ordinary *voirdupois* weights or a large set of gramme weights. Ordinary analytical gramme weights (Fig. 40) may be used for general assay and analytical purposes. Grain weights are also commonly employed; but for general use gramme weights are preferable. Two sets are needed, one ranging from a kilogramme to 1 gramme, and another from 50 grms. to a milligramme, or from 20,000 grs. to 20 grs. for rough weighing, and from 1000 grs. to 0.01 gr. for delicate weighings. For weighing silver prills a set of weights (Fig. 41), consisting of



FIG. 41.

10 grains with subdivisions in 1000 parts, or of 1 gramme similarly divided, is often employed; for gold, 5 grs. or 0.5 grm. divided in the same manner is employed.

Assay ton weights are also largely employed. A set ranging from 4 assay tons to $\frac{1}{30}$ assay ton is used for weighing out gold and silver ores.

For the value of the assay ton and its derivation, see p. 33.

WEIGHING.

In weighing, for weights under the centigramme (0.01 grm.) or the 10th of a grain (0.1 gr.), it is better to use the rider. This is a weight which slides on the beam of the balance. If the beam is divided into ten parts its effective weight is $\frac{1}{10}, \frac{2}{10}$; i.e. 0.1, 0.2 . . . 0.9 times its weight in the scale-pan at successive divisions from the centre. For example, a rider weighing 0.01 grm. (the usual weight) at division 5 exerts only the same effect as $\frac{5}{10}$ of its weight placed in the pan, i.e. 5 milligrammes or 0.005 grm.; at division 8, 8 mgrm. or 0.008 grm. Its position on the beam when equilibrium is established gives the third and fourth decimal places. With $\frac{1}{10}$ -grain riders, using grain weights, the second decimal place is given.

When the beam is divided into twelve parts a rider weighing 12 milligrammes is used, or 0.12 grains if grain weights are employed.

In weighing, the weights should be used in regular rotation, commencing with one too heavy and trying each in turn till equilibrium is established.

In manipulating the rider the balance case should be closed if an apparatus for moving the rider be attached.

All weights unused should be returned to their correct places in the box, the missing weights + the rider giving the weight of the article. This should be checked on returning the weights to the box.

Weights should not be handled, but moved with the weight tongs, or forceps, and should be returned to the box as soon as weighing is completed.

Sit well in front of the balance and adjust the light so as to shine clearly on the scale.

In watching the pointer follow its movements with one eye (the other being closed) to avoid parallax. Parallax may be avoided by fixing a small piece of looking-glass behind and above the scale. The eye is looking straight at the pointer when the reflection and the pointer are superposed. A mirror scale is even better.

The balance must be carefully levelled and calcium chloride or other desiccating agent kept inside the case.

The weights are generally put in the right-hand pan, and the substance to be weighed in the left.

Weighing out Substances.—First test the balance. In weighing out substances where a small indefinite quantity is taken, the powdered material, previously dried or otherwise, is put in a test-tube, or, better, a weighing-bottle (tube), A (Fig. 43), and the whole weighed. The portion for assay is then shaken out into a beaker and the remainder weighed. The difference in weight gives the amount taken.

In assay work more commonly a definite amount is weighed out, say 1 to 2 grms. To do this expeditiously two little scoops of copper foil (Fig. 42) should be made and very carefully balanced. In weighing, one is placed on the weight pan and the substance is weighed on the other.

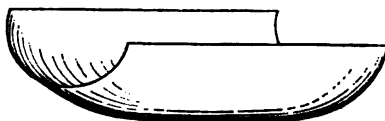
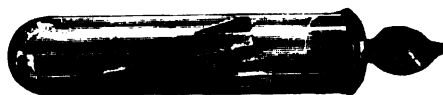


FIG. 42.

Never place anything on or take anything from the pan of the balance while it is swinging, and in lowering the beam or arresting the pans, wait till the pointer reaches the centre (if swinging), and then, by a steady and decided but not jerky movement, turn the cam and arrest it.

Do not wait for the balance to come to rest. Equilibrium is established and best indicated when the pointer swings to an equal distance on either side of the perpendicular.

Substances must be weighed cold. If hot, the heat may expand the arm of the balance while weighing, and a gradual increase in weight will be observed. The currents of hot air rising from a hot body will also interfere with the accuracy of the weighing. Substances which absorb moisture



A



B

FIG. 43.

must be weighed in weighing-bottles, or between watch-glasses, with spring clips, B, Fig. 43,* or else they may increase in weight. Keep the balance case closed except when adding or removing weights.

Assay Ton.—In the assay of silver and gold results are expressed in ounces per ton. For convenience of calculation the weights employed may be made to bear a definite relation to the ton. Thus a ton = 2240 lbs. If 2240 grains are taken each grain = 1 lb., and each grain of produce = 1 lb. per ton. If 224.0 grains are taken as the assay ton,

* From Newth's "Quantitative Analysis."

then each 0·1 of a grain produce = 1 lb. per ton of 2240 lbs. The American ton = 2000 lbs. If gramme weights are employed, 22·4 grms. may represent the ton, and each 0·01 gramme produce = 1 lb. The assay ton is a weight so selected and divided that an aliquot part represents 1 troy oz. per ton. It is thus derived : 1 lb. = 7000 grs., 1 ton = 2240 lbs., $\therefore 2240 \times 7000 = 15,680,000$ grs. = 1 ton. If troy ounces are required, then, since 1 oz. troy = 480 grs., $\frac{15,680,000}{480}$

= 32,666·6 troy ozs. = 1 ton ; hence if $\frac{32,666·6}{100} = 326·66$ grs. be

taken, each 0·01 gr. of produce = 1 oz. per ton. This weight is the assay ton in grains. If half an assay ton is taken the value of the produce must be doubled. Sets of weights consisting of assay tons in subdivision are often employed. Working with ordinary gramme weights the calculations are readily convertible, thus—

Since there are 32,666·7 ozs. troy per ton of 2240 lbs., if 0·01 grm. produce be taken to represent 1 oz., then $0·01 \times 32,666·7 = 326·667$ grms. must be taken, and if 0·001 grm. represent 1 oz., 32·667 grms. will represent the assay ton or full trial.

If the American ton of 2000 lbs. be taken, then on the same reckoning the assay ton will weigh 29·166 grammes.

REAGENTS USED IN DRY ASSAYING.

Reducing Agents.—1. **Carbon.** This is employed as powdered wood charcoal, or as lamp-black. When heated with it, most oxides are reduced to metal, carbon monoxide (CO) or carbon dioxide (CO₂) being formed according to the temperature at which the reduction takes place. In calculating the amount of charcoal required it should be assumed to contain 80 % pure carbon, to allow for moisture, etc., but it is better to make a blank experiment with litharge or red lead to ascertain its actual reducing value in cases where accuracy is required.

Carbon reduces some sulphates to sulphides, and some metallic sulphides partially to metal.

2. **Flour and Starch.** These substances are often employed instead of charcoal. They have about half the reducing power of carbon, but in some cases, especially those in which the substance to be reduced is distributed through a large bulk of material, the finely divided and more uniformly distributed carbon produced by their decomposition, is more satisfactory than charcoal.

3. **Argol, Tartar, White Argol, White Tartar, Cream of Tartar, Bi-tartrate of Potash.** $\text{KHC}_4\text{H}_4\text{O}_6$. This substance is largely employed. When heated it is decomposed and leaves a residue of potassium carbonate and finely divided carbon. The amount of the latter varies somewhat, but is about 15 % of its weight.

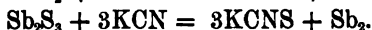
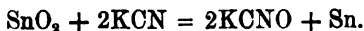
Argol is the name of the crude product deposited from wines during fermentation. It is sufficiently pure for most purposes in assaying, but sometimes contains sulphates which are objectionable.

4. **Black Flux** is a mixture of finely divided carbon and potassium carbonate obtained by mixing argol with from $\frac{1}{4}$ to $\frac{1}{2}$ its weight of nitre and igniting it with a red hot iron rod in a closed crucible. It was formerly much employed, acting both as a reducing agent and a flux, the reason for its preparation being to reduce the amount of free carbon left when the argol is heated, and thus increase the fusibility of the mass. Black flux absorbs moisture and should be kept in stoppered bottles.

Substitutes are now generally employed. They may simply consist

of undeFLAGRATED black flux, or a mixture of flour or starch with potassium or sodium carbonate. They contain from 6 to 30 % of flour.

5. **Potassium cyanide, KCN.** This not only acts as a reducing agent, but is a valuable flux. Heated with oxides it forms the cyanate KCNO and with sulphides the sulphocyanate KCNS.



The commercial salt contains much carbonate, usually only from 46 to about 50 % of cyanide being present. The quality of potassium cyanide has much improved in late years. For use in solution as a reagent, pure cyanide (gold cyanide) should be employed.

6. **Hydrogen gas** is sometimes employed as a reducing agent. A Kipp's apparatus (Fig 80) with an intervening drying bottle should be employed. The tube containing the sample should have a slight slope away from the apparatus.

7. **Carbon monoxide, CO,** is also occasionally used. It may be produced by heating yellow prussiate of potash with sulphuric acid in a large flask, but is most conveniently produced by packing a portion of the tube with charcoal nubs and putting a plug of asbestos to separate it from the assay. When the charcoal is heated, and air passed through, CO is formed.

8. When reducing agents of considerable density are required, powdered anthracite and coke dust may be employed.

Oxidizing Agents.—These are employed for the purpose of removing sulphur in assaying copper and other ores and to diminish the reducing power of ores in silver and gold assaying, as well as for simple oxidation.

1. **Nitre, Potassium nitrate, KNO₃.** This is almost the only oxidizing agent commonly employed. It should be used in fine powder and intimately mixed with the assay, except when employed in refining metals. The quantity of nitre required to counteract the reducing power of various sulphides is given below.

QUANTITY OF NITRE REQUIRED.

Name of Substance.	Parts.	Quantity of Nitre.
Iron pyrites	1	2½
Galena	1	½
Antimonite	1	1½
Copper pyrites	1	2½
Zinc blende	1	1½

2. **Potassium chlorate, KClO₃,** is also sometimes employed.

3. **Red lead and litharge** act as oxidizing agents in assaying sulphurous gold and silver ores and also furnish lead for concentrating the precious metal.

Fluxes.—The term is here restricted to substances added solely or principally to produce fluidity of the assay.

1. **Sodium carbonate**, Na_2CO_3 . When heated to bright redness this fuses to a somewhat viscous liquid. It decomposes silicates, and combines with silica, forming a fusible silicate of soda. Used alone, or in conjunction with potassium carbonate or other fluxes to increase fluidity, it forms a most useful reagent for removing siliceous gangue. The dry carbonate Na_2CO_3 (not the crystals $(\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O})$), or the bicarbonate NaHCO_3 , should be used. The fluxing power of the bicarbonate is only one-half that of the normal carbonate. One part of silica requires roughly about $1\frac{2}{3}$ times its weight of Na_2CO_3 , and $2\frac{2}{3}$ times its weight of bicarbonate, to produce Na_2OSiO_2 . Soda ash may be used.

2. **Potassium carbonate**, K_2CO_3 . This is sometimes used alone, but more often in conjunction with sodium carbonate. The mixture is more fusible and produces greater fluidity than when either salt is used alone : 10 parts of sodium carbonate are mixed with 13 parts of the potassium salt.

3. **Lime**, CaO , is used as a flux for silica and silicates such as clay (aluminium silicate). If these are absent, glass or china clay is often added, as well as lime, to produce a compound fusible silicate.

4. **Magnesia**, MgO , is rarely employed as a flux.

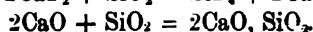
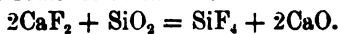
5. **China clay**, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, is used in conjunction with lime for fluxing substances containing much free silica.

6. **Glass** is used as a flux and also as a fusible covering. Glass free from lead should be employed.

7. **Lead glass**. Silicate of lead. This is used instead of litharge for fluxing substances free from silica and metallic oxides soluble in molten litharge. It is made by melting white sand with 4 to 5 parts of litharge.

8. **Litharge** and **red lead** are used as fluxes in the assay of silver and gold ores. They act as fluxes for silica, and also as solvents for any metallic oxides present, and prevent an undue amount of base metal being reduced and passing into the lead obtained. Red lead also acts as an oxidizing agent, litharge being produced. They also by their reduction furnish the metallic lead required to concentrate the precious metals. See Silver Assay.

9. **Fluor spar**, calcium fluoride, CaF_2 , is fusible alone. It is used as a flux for lead, calcium, and barium sulphates, and phosphate of lime (bone ash, apatite, etc.), which it dissolves, forming readily fusible compounds. It also removes silica thus—



In this case it is used in conjunction with other fluxes. Slags containing fluor spar are usually brittle. This tendency is increased by sudden quenching.

10. **Silica** is employed as crushed quartz, or as white sand. Quartz is much more readily crushed if previously heated to redness in a muffle and plunged into cold water. Silica is used as a flux for ores containing basic substances, *e.g.* limestone (calcium carbonate), etc., in conjunction with clay or alumina, or sodium carbonate.

11. **Borax**, $\text{Na}_2\text{B}_4\text{O}_7$. This is one of the fluxes most commonly employed. It must be dry (not crystal, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), or in the form of glass. Borax melts to a clear liquid and readily dissolves, earthy and other metallic oxides forming complex borates. It also fluxes silica. The soda combines with the silica, and the boric acid liberated is of itself fusible, and may serve for fluxing metallic oxides.

12. **Common salt**, NaCl . This substance melts at a red heat, and is very fluid when molten. It is employed (*a*) as a covering flux to exclude air, as its low specific gravity when fused keeps it at the top of the assay—its liquidity tends to prevent the boiling over of an assay; (*b*) in admixture with other bodies when extremely fluid slags are required. At high temperatures it volatilizes, and there is some tendency to form volatile metallic chlorides and occasion loss. It should be dried before use.

13. **Potassium bisulphate**, acid potassium sulphate, KHSO_4 , is used to some extent as a flux. Refractory aluminous and other ores are sometimes melted with it as a preliminary operation in their analysis, the sulphuric acid liberated at a high temperature effecting their decomposition more readily than the acid in solution. It may also be employed as a sulphating agent in roasting processes and in admixture with salt (sodium chloride) in chloridizing roasting.

14. **Refining or white flux** (see Copper, p. 76).

15. **Oxide of iron** is sometimes used for fluxing silica. It is employed in the form of red hematite mixed with carbon to reduce it to the ferrous state. $\text{Fe}_2\text{O}_3 + \text{C} + \text{SiO}_2 = 2\text{FeO} + \text{SiO}_2 + \text{CO}$.

Sulphurizing Agents.—These are employed to introduce sulphur for the purpose of concentrating copper, lead, or other metal in the form of a matte, or occasionally for removing these metals in that form.

1. **Sulphur** is used in the form of flowers of sulphur.

2. **Iron pyrites**, FeS_2 , is the substance most commonly employed. It must be free from copper pyrites and galena. The matte obtained is a mixture of iron sulphide with other sulphides. A mixture of red hematite and sulphur may be used as a substitute.

Desulphurizing Agents.—1. Iron is employed in the reduction of

lead ($\text{PbS} + \text{Fe} = \text{FeS} + \text{Pb}$), antimony, bismuth, and other sulphides. It does not completely reduce copper sulphide. The iron is best employed in rods with flattened ends, or in U-shaped bent strips, which can be readily removed from the material while molten. Iron crucibles are also employed. If filings or turnings are used, the amount required should be carefully calculated, as it is impossible to remove any excess.

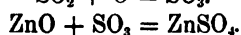
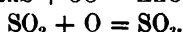
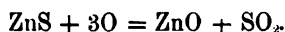
2. **Hammer scale**, Fe_3O_4 , or hematite, Fe_2O_3 , mixed with carbon for its reduction is sometimes used.

3. **Copper** may also be employed.

4. **Sodium and potassium carbonates** and **potassium cyanide** also act as desulphurizing agents.

5. In removing sulphur from sulphates, carbon, or some other reducing agent, must be employed to remove the oxygen, in conjunction with iron or other desulphurizer.

Sulphating Agents.—Many sulphides yield normal or basic sulphates when roasted. This action is promoted (1) by roasting at a low temperature, (2) the presence of silica and other inert bodies, and (3) by a copious air supply. In these cases the sulphate is formed (a) by the direct combination of the sulphide with oxygen; (b) by the SO_2 , produced by the oxidation of the sulphur uniting with free oxygen under catalytic influence, and the resulting SO_3 combining with the oxide of the metal (also formed during calcination), to form sulphate, thus—



Bismuth and antimony sulphides do not yield sulphates when roasted.

1. **Ferrous sulphate**, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is employed for providing sulphuric acid in roasting. When heated it splits up, yielding oxide of iron, sulphurous and sulphuric anhydrides. It is better if partially dried before use.

2. **Sodium and potassium bisulphates** (nitre cake, NaHSO_4) are also useful for the same purpose.

Chloridizing Agents.—1. **Common salt**, NaCl , is the only reagent generally used for this purpose. If the material treated be not a sulphide, iron pyrites, sodium bisulphate or similar compound should also be added.

2. **Chlorine gas** is used for chlorinating. It may be generated by heating manganese dioxide with strong hydrochloric acid in a separate vessel, or, in chlorinating ores, from bleaching powder and sulphuric acid in the chlorinating vessel.

Granulated Lead.—This is made by melting a quantity of pure lead (reduced from red lead with charcoal only) in a crucible, and allowing it to cool in the pot until it no longer chars a stick put in the metal. It is then poured into a stout wooden box, about 15 ins. by 10 ins. by 7 ins. deep, the inside of which has been slightly blacklead, and, when just on the point of solidifying, violently shaken with a somewhat rotary motion so as to throw it into contact with the sides of the box. The hot lead breaks up into small particles, and the shaking is continued for a few moments. The resulting mixture of fine and coarse particles is sifted through a 12 s. sieve, and the coarser particles remelted, with fresh additions of lead, for granulation.

WET PROCESSES.

Solution is conducted in beakers, flasks, or evaporating dishes, according to circumstances. Vessels should, as far as possible, be kept covered. For covering beakers, clock-glasses answer best. Flasks should have a small funnel placed in the neck, and if spurting occurs they may be inclined. Evaporating dishes are best covered by inverting over them a funnel, from which the stem has been cut. All covers must be rinsed into the solution with water or acid, as circumstances warrant. In dissolving and evaporating, beakers and flasks are best heated on a hot plate (see Fig. 35), being moved nearer to or further from the flame as may be required. In drying an evaporation it may be necessary to move the beaker to the cooler part of the plate. Evaporating dishes, if flat-bottomed, may be similarly dealt with, but if round-bottomed a sand bath should be used. Where necessary (which is not often, if the use of a hot plate be understood), a water bath may be employed. A good substitute is to place the dish on the top of a wide flat beaker, having a lip. Water is placed in the beaker and boiled, the lip serving as a vent for the steam.

Fig. 44 shows a collection of convenient vessels for boiling and evaporating purposes, etc.

(a) **Bohemian Flasks.**—The most useful sizes are 4, 8, 12, 20, and 40 ozs.

(b) **Conical (Erlenmeyer) Flasks.**—The most useful sizes are 5, 10, and 20 ozs. This is the most useful form of flask for most purposes. It does not afford lodgment for solid matters in pouring, and can be washed out readily.

(c) **Parting Flasks** for treating buttons of gold and silver with nitric acid.

(d) **Beakers of various shapes.**—The tall form is convenient for evaporating on a hot plate. The wider form boils more rapidly. The conical form is useful for ready handling. The most useful sizes are Nos. 1–8.

(e) **Porcelain Evaporating dish.**

(f) **Funnels.**—These should be accurately pitched to 60°. Test with a folded filter, and reject those which are not satisfactory. Sizes varying from 2½ to 7 ins. in diameter are convenient. They may be ribbed or plain. For use with filter pump plain funnels must be used.

(g) **Wash-bottle.**—This is the ordinary form, but the position of the jet should be such that when the neck is grasped in the hand it

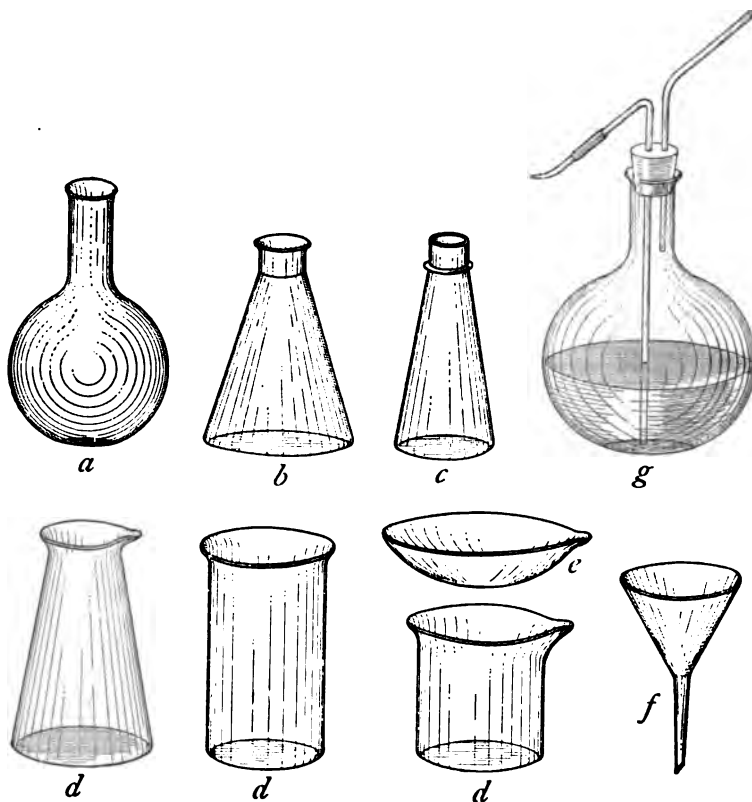


FIG. 44.

can be easily reached and guided by the forefinger. By causing the jet to turn up slightly, as shown, it may be very conveniently used for washing out beakers into filters, and yet serve for ordinary purposes.

Bunsen Burners.—Of these two forms are used: (1) the ordinary tall Bunsen (Fig. 45) provided with chimney (a) and support (b), earthenware draught shield (c), rose (d), and, for blowpipe work, a

jet; (2) the argand form (Fig. 46). The latter is most convenient for ordinary boiling purposes.

A long form of Bunsen is used for heating the hot plate (see Fig. 35). Spirit-lamps, or burners burning spirit vapour or benzol, may be employed in place of gas burners. As a support for beakers and flasks, asbestos millboard, or brass wire gauze, is convenient; but sand plates or baths may be employed. Water baths should be made of copper or cast-iron.

Retort (ring) stands and **iron tripods** are necessary for supports. The former should be provided with screw clamps. Clay triangles for supporting crucibles over the flame should also be provided.

Crucibles.—Platinum crucibles are almost indispensable for some

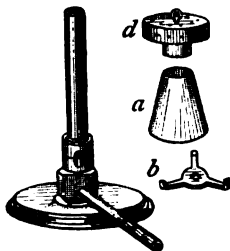


FIG. 45.

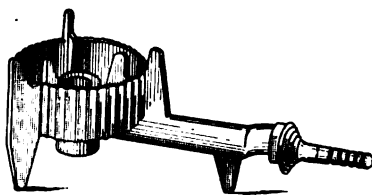


FIG. 46.

purposes. They should be carefully preserved. The best plan is to have a wooden plug turned and polished to accurately fit the new crucible, on which the crucible can be kept when not in use, or a plaster cast may be taken and used for the same purpose. For cleaning purposes Calais sand is best. Porcelain crucibles are often required, the wide form being more satisfactory for most purposes. Rose's crucible (see Fig. 88) is used for igniting precipitates in an atmosphere of hydrogen or other gas.

Air and water ovens for drying precipitates will be required, the former for dealing with precipitates, which do not alter by heating above the boiling-point of water, and the latter for drying at 100° , where such changes do occur, or where heating at this temperature is necessary.

Desiccators will be required, into which dried precipitates or crucibles after ignition can be placed to cool before weighing.

Of incidental apparatus for various purposes the following will be required :—

Glass tubing and rod, various sizes; test-tubes, $5'' \times \frac{3}{4}''$ is a convenient size for ordinary use, but other sizes should also be kept;

test-tube rack; clock-glass covers of various sizes for beakers; round and triangular files; cork borers for ordinary corks; small tongs for porcelain crucibles, similar to *d*, Fig. 18; wooden filter stands; burette stands; tube brushes; indiarubber tubing of various sizes; fine wire for securing rubber connections; pencils for writing on glass to mark vessels in which operations are being conducted; camel-hair brushes; corks, assorted; watch-glasses; glass bottles for reagents; thermometers; platinum and clay triangles; Daniell's or other form of constant battery cell, 4-quart Daniell's cells answer very well; platinum electrodes (see Figs. 61 and 62); combustion furnace (Fig. 89); combustion tubes of glass and porcelain; calcium chloride tubes and drying towers; potash bulbs; agate and porcelain mortars.

Other apparatus applied to special purposes is described below or in connection with the operations for which it is employed.

Consult the catalogue of a good chemical dealer in connection with the above list. A list of materials and apparatus for taking abroad is given in Appendix A.

Evaporation.—This commonly follows solution. For assaying purposes it may, in most cases, be very conveniently conducted in the beaker in which solution is effected, the clock-glass being removed when the action has ceased and the beaker placed on the hot plate so as to boil gently down without spurting. When the bulk is small and the solution syrupy, great care must be exercised in moving the beaker towards the flame to avoid loss and fracture of the beaker. Evaporating dishes are, in many cases, more expeditious, but require constant stirring during the evaporation, or loss will occur. In other respects they are more tedious, as the transferring, washing out, etc., and subsequent evaporation of liquid used for this purpose often makes the operation longer.

Filtration.—The filter paper employed varies with requirements. Ordinary English or German paper suffices for common filters, where the precipitate is to be rejected or re-dissolved. Munktell's Swedish, or some equivalent paper of uniform character, with a known quantity of ash, or ashless papers (papers which have been treated with hydrochloric and hydrofluoric acids) should be used where precipitates are to be weighed after burning.

Sometimes precipitates are detached from the paper after drying and weighed without ignition. Smooth papers must be used in such cases.

In buying paper in sheets, square sheets are more economical than oblong.

NOTE.—Round filters are folded into four, opened with three thicknesses on one side and one on the other, and dropped into the funnel.

The liquid should be poured on to the filter, down a glass rod placed in contact with the side of the vessel. Filtration through paper may be hastened by means of a suction tube attached to the funnel stem as shown (Fig. 47), but the paper must fit the funnel tightly. Such appliances are not to be recommended for quantitative work.

Rapid filtration is best effected by the employment of filter pumps. Various forms are employed (see Fig. 48). The suction tube is connected with a stout flask or bottle, preferably having a tubulure at the side, by specially thick indiarubber tubing, and the stem of the funnel passes through a rubber cork, or well paraffined ordinary cork. When filter pumps are employed, specially stout paper manufactured for the purpose must be used, or, if ordinary paper be used, a platinum, or perforated porcelain or parchment cone which fits the bottom of the funnel must be employed, or the suction will tear the paper.



FIG. 47.

NOTE.—Platinum cones are made of stout foil, being bent on a plaster cast of the inside of the funnel, which must be plain, not fluted. The foil is cut thus (Fig. 49), so as to give a slight overlap. It need not occupy more than $\frac{1}{4}$ to $\frac{3}{8}$ of an inch of the funnel.

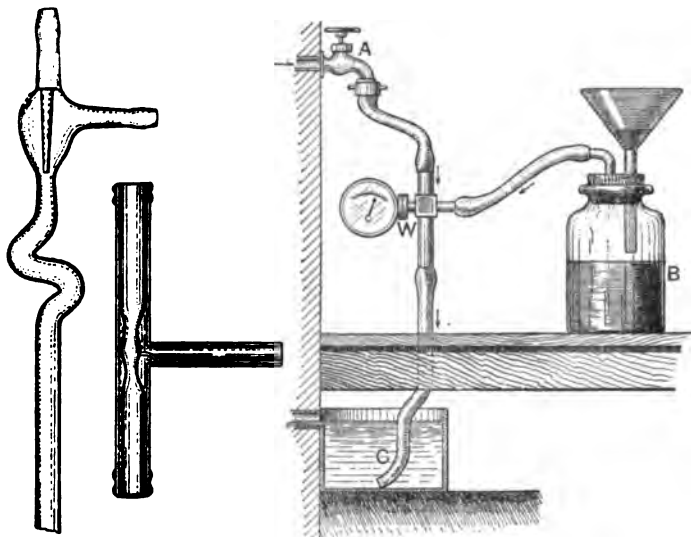


FIG. 48.

For filtering bulky gelatinous precipitates, Hirsch's porcelain funnels, with flat perforated bottoms, which are covered by a circle of filter

paper may be used with advantage (Fig. 50). The grid is at G. There is some little trouble in washing the precipitate. Perforated porcelain plates for fitting into ordinary glass funnels may also be obtained.



FIG. 49.

Asbestos and Sand Filters.—In some cases paper filters are not admissible, owing either to the necessity of excluding organic matter, as in the estimation of carbon in iron and steel, or because they are acted on by the

solution. Asbestos or other material is then used. If simple filtration be required, and the precipitate is not too fine, an ordinary funnel, or, better, one of special form, with a bulb at the top of the stem (Fig. 86, p. 336), may be plugged with glass wool and a layer of silica sand, say $\frac{1}{4}$ in. deep, placed on top.

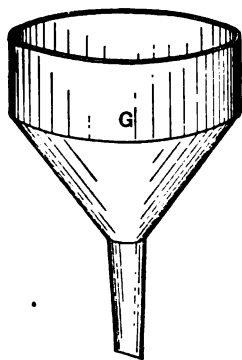


FIG. 50.

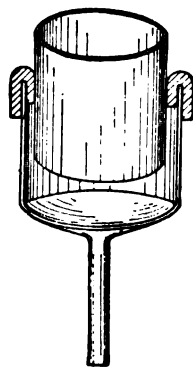


FIG. 51.

Asbestos Filters.—The asbestos employed should be of the best quality, finely fibrous and free from soapstone. It should be gently ignited and then ground with water in a porcelain mortar to a pulp. With an ordinary funnel the stem should be plugged with glass wool, a layer of dry asbestos $\frac{1}{4}$ inch thick laid on the top, and the surfaces flattened with the finger. A little of the pulp should then be poured in, sufficient to form a layer $\frac{1}{8}$ inch thick and the water allowed to drain off; for safety a little white sand may be placed on the top of the asbestos. The sand should be moistened with NH_4NO_3 , and ignited before use.

Special capsules for asbestos filters are also employed. A glass funnel, of the shape Fig. 51, has a porcelain capsule, with a very finely perforated bottom, which fits into it. A rubber band round the top

makes it air-tight. Asbestos filters require a filter pump, or they work exceedingly slowly.

Washing.—This is an important operation. A number of washings with smaller quantities of liquid are more effective than a few with larger quantities. To use the minimum of liquid, let each addition drain through completely before adding more. Sometimes with very gelatinous precipitates this is very tedious. It can be got over when only the filtrate is required at the sacrifice of very little accuracy by taking twice as much of the body for analysis as is really required, dissolving and proceeding as usual up to the point of filtration. The solution is then diluted to a known volume, say 500 c.c., and filtered (at 60° Fahr.) through a paper not previously wetted into a 250 c.c. flask, the first 250 c.c. coming over being used for the determination. The final calculation is made on half the material first weighed out. The precipitate and remaining liquid can then be discarded.

In washing, the edges of the paper should never be allowed to dry, but should be kept constantly wetted, or the air-action may lead to the formation of insoluble salts by oxidation in the paper, especially in acid solutions. This will necessitate moistening the edges with fairly strong acid. A dropping-bottle should be used for this purpose.

Titration and the use of Burettes.—Various forms of burette are shown in Fig. 52. Those with indiarubber connections are unsuitable for permanganate and iodine. Tap burettes are best. The form with a projecting tap is most convenient, if a burette-stand with a wide base be used.

Convenient sizes are 100 c.c. graduated in $\frac{1}{2}$ c.c., *i.e.* to 0.2 c.c. and 50 c.c. graduated to $\frac{1}{10}$ c.c.

Filling the Burette.—Wash out the burette and drain it. Then pour in a few c.c.'s of the solution and shake it up well. Allow a little of it to run through the tap or delivery jet, and then pour away. Repeat this. The burette may also be prepared by thoroughly drying it after washing. This is done by washing it out with alcohol, then with ether, and blowing air through from the bellows to remove the

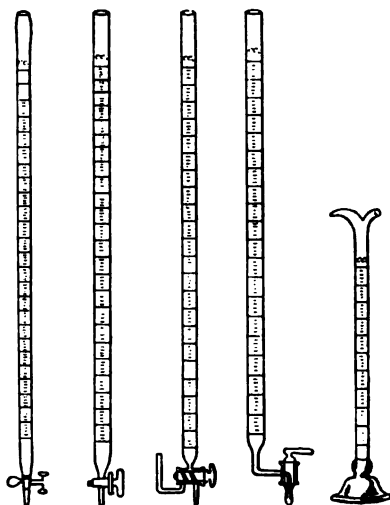


FIG. 52.

ether. Then fill up with the solution above the mark, and run down to the 0 c.c. mark.

In works where burettes are kept for a particular purpose, the filling may be effected in other ways. In Fig. 53, SB is the stock-bottle containing the standard solution, and T a glass syphon tube which passes nearly to the bottom of the bottle, and connects with the burette at J through tap or pinch-cock. B is a blowing-tube by which T is first filled (P being open). The liquid rises in the burette, and is stopped

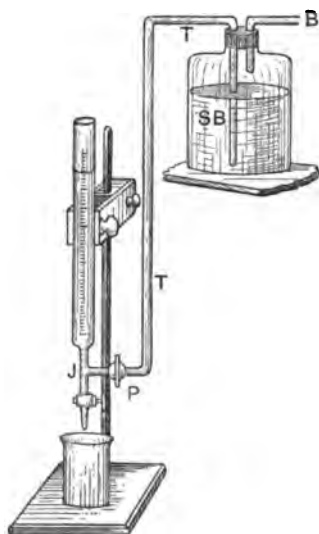


FIG. 53.

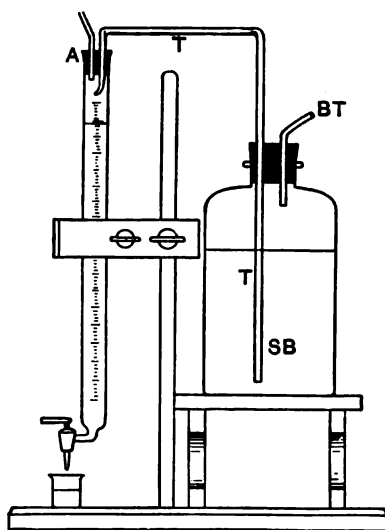


FIG. 54.

when it is full. After using one burette full, if P be opened, the solution is syphoned over into the burette.

Fig. 54 shows a method by which the stock-bottles are kept at a low level. The syphon tube dips to the bottom of the bottle, and the end A is drawn out a little and adjusted to the meniscus level of the liquid in the burette. The solution is blown over by BT, any excess drains back into SB.

Titration is the act of adding the solution required to bring about the desired reaction. Shaking or continuous stirring should accompany the addition of the solution. Reactions depending on change of colour are generally best conducted in a large white evaporating dish, especially if precipitates are present. The vigorous stirring possible assists in the settling of the precipitate, while the white dish shows up the colour.

If by mischance too much of the standard solution is run in, a few c.c.s of a solution of the metal of known strength may be added, the titration continued, and in the calculation the amount of metal thus added deducted. In some cases a portion of the assay solution is kept back for this purpose, and added before finishing the titration.

In reading burettes, the measurement is taken at the lowest point of the meniscus (the curved surface of the liquid in the tube). To prevent error, the eye must be brought level with this point. If read from above in the direction A (Fig. 55), too low a reading will be obtained, owing to parallax; if from below, in the direction B, too high a reading. The divisions of the burette are more plainly seen if a white paper be held behind so as to reflect the light up and through the burette. Erdmann floats may be used if preferred (Fig. 56).

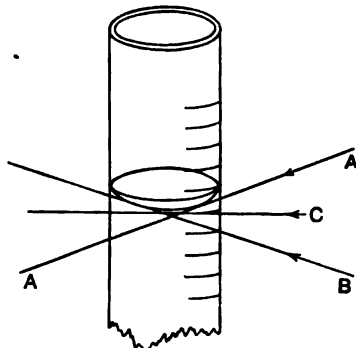


FIG. 55.

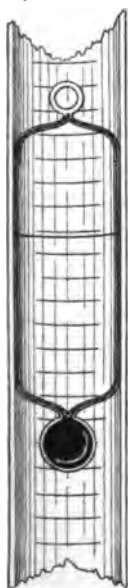


FIG. 56.

Measuring Cylinders and Flasks.—Graduated cylin-

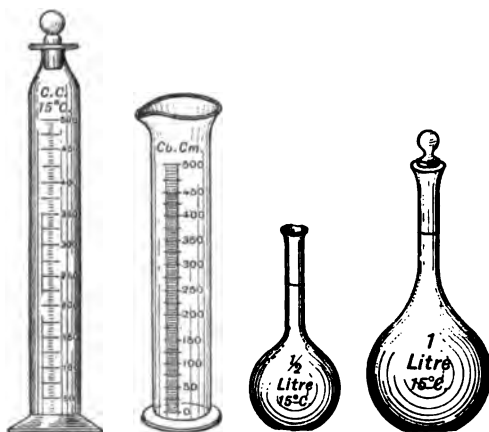


FIG. 57.

ders (Fig. 57) are convenient for measuring acids, etc., and in the preparation of solutions; convenient sizes are 50, 100, and 200 c.c. The stoppered form may be used instead of a flask for making up solutions.

Graduated flasks of varying capacity from 100 c.c. to 2 litres are required for making up solutions to a known volume (Fig. 57).

Making and Keeping Standard Solutions.—The substance to be dissolved is weighed accurately on a watch-glass, and dissolved in water in a beaker with the aid of heat when necessary, transferred to a measuring flask, the beaker well washed, and the solution diluted with distilled water up to the mark. The temperature of the solution should be 60° Fahr. If hot, it must be allowed to cool before diluting, and if cold before finishing the dilution, it must be allowed to attain the temperature of the laboratory. Shake up well to mix the solution. Transfer to a clean, dry, Winchester bottle, label, and add a blank label to receive strength and value when determined.

Standard solutions are best kept in a cool dark corner of the laboratory. Solutions which are oxidizable, such as sodium thiosulphate, potassium cyanide, etc., or liable to alteration, must be examined frequently. Of common standard solutions sodium thiosulphate (hypo-sulphite), potassium cyanide, potassium permanganate, stannous chloride, iodine, ferrous sulphate and potassium ferrocyanide are most liable to alteration. Cyanide should be examined from day to day, sodium thiosulphate, iodine, ferrous sulphate (even if acidulated), and stannous chloride, should be standardized at least weekly. Permanganate and ferrocyanide solutions will keep a fortnight without perceptible change.

Solutions of bichromate of potash, and similar stable salts do not alter, except by evaporation.

Solutions of substances for addition at the end of titration should be made under the same conditions as the solution to be assayed, and contain say 0.01 grm. of the substance per c.c., and should be distinctly labelled.

Indicators.—Solutions used for determining the end of reactions are often best made as required.

Uranium acetate solution for ferrocyanide, the mercuric-platinic chloride solution for stannous chloride, and the sulphocyanate indicator may be made up and kept, but ferricyanide of potassium for iron determinations, and starch for iodine and thiosulphate titrations must be made as required, or only kept a short time.

Standardizing is the operation of determining the value of a solution in terms of a given substance. Thus the value of a solution of sodium thiosulphate may be expressed in terms of copper—

$$1 \text{ c.c.} = 0.00744 \text{ grm. Cu,}$$

meaning that every c.c. of this solution added to a solution of copper, prepared as on p. 85, in the process of titration, is equivalent to that

quantity of copper in the solution. All standardizing operations are trials conducted on weighed quantities of a pure substance or one of known composition in a manner identical with that followed in the actual assay, and under similar conditions.

Example.—0.5 gm. of pure copper is weighed, dissolved, and the solution prepared, and titrated (see p. 86). If it takes 67.2 c.c. of the "hypo" solution, then $67.2 \text{ c.c.} = 0.5 \text{ gm. Cu}$ and $1 \text{ c.c.} = \frac{0.5}{67.2} = 0.00744 \text{ gm. Cu}$. If in titrating a solution with this standard "hypo" 40 c.c. are employed, then $0.00744 \times 40 = 0.2976 \text{ gm.}$ of copper in the solution, and if 5 grms. of the material to be tested had been dissolved, then the 5 grms. contained 0.2976 gm. Cu, and the percentage $= 5 : 100 :: 0.2976 = 5.952 \% \text{ Cu}$.

In works it is convenient for testing purposes to use standard solutions of constant value, and tables of references are constructed on that assumption. A convenient standard is $1 \text{ c.c.} = 0.01 \text{ gm. metal}$. The method of adjustment is as follows:—The standard solution is first made of a little greater strength than required, and standardized. If its value is, say, 0.0107 gm., 1 litre—1000 c.c.—instead of being equal to 10 grms. is equal to 10.7 grms. of the metal, that is, 0.7 in excess. If now 70 c.c. water per litre of solution remaining be added, there will be 10.7 grms., equivalent in 1070 c.c. of solution and $\frac{10.7}{1070} = 0.01 \text{ gm.}$

Therefore, for every 0.1 in excess of 10 grms., add 10 c.c. of water; for every 0.01 gm., add 1 c.c.; for every 0.001, add 0.1 c.c. per litre.

Pipettes are employed to remove the portion of a solution required for analysis to the vessel in which the operation is to be carried out. They are graduated to deliver fixed quantities of solution. They have usually one mark on the stem (Fig. 58), and are filled by putting the end in the liquid and sucking out the air. The liquid is prevented from running out by covering the upper end with the forefinger. By carefully relieving the pressure, the excess of liquid is allowed to escape down to the mark, and the measured quantity dealt with as desired. Pipettes may be provided with taps, and in some cases are graduated to deliver varying amounts of solution, after the fashion of a burette. Before using pipettes should be rinsed out with the solution to be measured. Convenient sizes are 5, 10, 25, 50, 100 c.c.



Fig. 58.

Drying Precipitates.—This may be done in the funnels in an ordinary air bath unless the precipitate undergoes alteration if overheated. In that case a water-jacketed oven is employed. The space under the hot plate, if tiled, may be advantageously employed, the paper being opened out and placed flat. With a little care and experience the temperature of various positions can be very well gauged.

Precipitates, to be dried at any given temperature, are weighed on tared filters. The ordinary method of drying a paper and then weighing

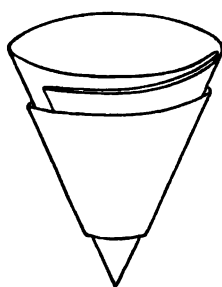


FIG. 59.

it before collecting the precipitate, which after drying is weighed on it, is open to objection, but is generally the best. Another method is to take two papers and dry them, fold as for filtering, cut off the bottom of the cone of one (Fig. 59), and then balance one against the other by clipping the perfect paper round the edge. The two papers are then placed in the funnel, the imperfect one next the glass, the filtration, washing, and drying proceeded with, and in weighing one paper is placed on one pan with the weights, and

the other with the precipitate on the other. This method cannot be adopted with fine precipitates which have a tendency to pass through the paper. In such cases a previously dried paper must be employed.

Igniting.—A sheet of glazed paper is spread on the bench. The filter paper is removed from the funnel, and the precipitate, detached as far as possible by bending the paper, is turned out on the glazed paper and covered by the funnel. The filter paper is then wrapped up and burnt, either held in platinum wire in the Bunsen flame, the ash falling into a weighed crucible, or in a platinum or porcelain crucible supported on a triangle, over a good Bunsen, or, better, the crucible containing the paper, folded closely, is placed in a muffle at a cherry red heat, or the burning may be commenced over a Bunsen and completed in the muffle. The heating is continued till all the carbonaceous matter has burnt away. The temperature must not be sufficient to melt the substance or cause it to attack the glaze if porcelain crucibles are employed. The ash is then treated, if necessary, to reconvert any reduced precipitate back to its original form.

Many precipitates, *e.g.* lead sulphate and silver chloride, are reduced when heated with carbonaceous matter. After removing the bulk of the precipitate as directed above, the paper is carefully folded and burnt over a Bunsen burner, the ash being received on the lid of the crucible. Any reduced metal mixed with the filter ash may then be reconverted by treating the ash with a few drops of nitric acid and

warming, then, adding a drop of sulphuric or hydrochloric acid and carefully evaporating quite dry.

The bulk of the precipitate is then brushed into the crucible, heated to redness, cooled in a desiccator, and weighed when quite cold.

Weighing.—For rules of weighing, see p. 32. The weight of the crucible deducted from the total weight = weight of compound + ash of paper, which must be deducted.

Weight of crucible + precipitate	=	25.389
„ „ „ „	=	25.120
Weight of precipitate + ash of filter	=	0.269
„ ash „ „	=	0.005
Weight of precipitate „ „	=	0.264

Use of Factors.—The factor for any substance represents the amount of the substance present in or equivalent to one part of the precipitate weighed or body determined; *e.g.* factor for lead in $\text{PbSO}_4 = 0.6829$.

It is arrived at thus—

$$\begin{aligned} \text{PbSO}_4 &= 206.4 + 32 + (4 \times 15.98) = 302.24 \\ \therefore \frac{206.4}{302.24} &= 0.6829. \end{aligned}$$

When, therefore, the weight of a precipitate is multiplied by “a factor,” the result is the weight of the substance (whose factor is employed) contained in the precipitate. From this weight the percentage in the substance assayed is calculated.

Blank Determinations are made for the purpose of determining (a) the purity of the reagents used, to ensure their freedom from the metal sought, or (b) the influence of the operations on the accuracy of the determination. In the first case, if any be found, it will be necessary to reject the reagent, or having determined the amount it contains, to use it in measured quantities, in order that a deduction can be made to allow for it. In the second case blanks are used in silver and gold assays to determine the effect of the operation on the contained precious metal. (See pp. 111, 150.)

Marking.—All flasks and beakers into which an assay passes should be similarly marked. Useful marking-leads which write on glass can be obtained, and there is no danger of the identifying marks being lost. They are also easier to remove than labels.

PART II.

1

2

LEAD.

THE estimation of this metal is generally required in the following substances :—

Ores and products containing the metal.

Class 1. Sulphurized materials, galena, lead mattes and certain classes of slags.

Class 2. Oxidized ores and products.

Class 3. Metallic products.

Lead Ores.—*Class 1. Galena, blue lead ore.* Sulphide of lead, PbS . This mineral has a high metallic lustre, and a bluish lead grey colour. It is very heavy (sp. gr. 7·35—7·7), hardness 2·5 (a little softer than marble), and is very brittle. It crystallizes in cubes, octahedra, and other cubic forms. The cleavage is cubic and very perfect. Heated before the blowpipe on charcoal, it decrepitates, fuses, gives off sulphur dioxide (SO_2), and finally yields a bead of lead with a yellow incrustation on the charcoal. Cleavages may be large or much broken up.

Minerals more or less resembling galena. Antimonite, bournonite, argentite. Zinciferous galena resembles ordinary galena, but the lustre is greyer and the specific gravity lower.

Anglesite.—Sulphate of lead, PbSO_4 , is a heavy white mineral, crystallizes in rhombic forms, is softer than cerussite, and has a sp. gr. 6·1—6·4. Before the blowpipe, with sodium carbonate, it yields a lead bead with effervescence.

Other minerals, consisting of mixtures of carbonate and sulphate and chloride of lead occur.

Class 2. Minium.—Red lead, Pb_3O_4 , is red and pulverulent, and is not important.

Cerussite.—White lead ore, carbonate of lead, PbCO_3 . The colour is white, tinged with grey, yellow, or brown. It occurs crystallized in rhombic forms with a vitreous lustre, and also massive, or earthy. Its hardness varies from a little below 3 to 3·5, and the sp. gr. 6·46—6·48. It is associated with other lead ores. Before the blowpipe it decrepitates, and readily yields a button of lead with incrustation on the charcoal. It effervesces in dilute nitric acid on warming.

Pyromorphite.—Linnetts, green lead ore, $3(\text{Pb}_3(\text{PO}_4)_2)\text{PbCl}_2$. The colour varies from green to brown, and is sometimes yellowish. The ore occurs crystallized in hexagonal forms, and massive. It is a little softer than fluor spar, 3·5—4; and is heavy, sp. gr. 6·5—7·1. It occurs associated with other lead ores. Before the blowpipe it melts, gives a bluish flame (PbCl_2), and with carbonate of soda gives before the blowpipe a bead of lead with yellow incrustation on the charcoal.

Mimetite, Mimetesite.—Arsenate of lead, closely resembles pyromorphite. Its colour is usually paler—white, pale yellow, and light brown tints prevailing.

Cromfordite and Matlockite are mixtures of chloride and carbonate. **Leadhillite** is a mixture of sulphate and carbonate; rhombic, cleavable; the laminae are flexible. **Wulfenite** is the molybdate of lead, citron yellow to orange red. Tetragonal. Hardness, 2·75—3. Waxy. Heavy. **Crocoisite** is the chromate of lead; monoclinic, orange red. Hardness, 2·5—3. Yields lead before the blowpipe.

Products.—*Class 1.* **Lead mattes** approximating more or less in composition to galena. **Grey slag** from reverberatory furnace smelting a greyish friable mass, frequently containing distinct enclosures of lead sulphide and carbon. The grey slag from the ore hearth is black. **Calcined ore** for blast furnace smelting containing sulphide, sulphate, and oxide.

Class 2. **Drosses and Abstriches** from improvement of hard lead. **Cupel bottoms**, etc. **Skimmings** from Pattinson and other pots. **Slags** containing lead, as silicate.

Class 3. **Work lead, Hard lead.** **Residues** from liquation processes, **Antimonial lead**, etc.

CHEMICAL REACTIONS OF LEAD.

Dry Tests.—1. The finely powdered substance, moistened with hydrochloric acid, and heated in the outer flame of the Bunsen on a thread of asbestos tinges the flame bluish.

2. A little of the powder mixed with four times its bulk of fusion mixture, and heated on charcoal, in reducing flame before the blowpipe yields a bead of lead which marks paper, and a yellow incrustation.

Wet Tests.—The substance under examination is dissolved in water, nitric acid, or other solvent, the excess of acid removed by evaporation and the insoluble matter filtered off.

Portions of the solution are then tested by adding—

1. Hydrochloric acid. If the solution is cold and sufficiently concentrated, a white precipitate of PbCl_2 falls, which dissolves on diluting largely, or on heating.

2. Potassium iodide. A yellow precipitate of PbI_2 falls, soluble on boiling. On cooling the lead iodide crystallizes out in glistening spangles.

3. Potassium chromate produces a yellow precipitate of lead chromate, $PbCrO_4$, soluble in excess of caustic soda.

4. Sulphuric acid yields a white precipitate of lead sulphate, $PbSO_4$, nearly insoluble in water, less soluble in dilute sulphuric acid, and insoluble in alcohol. It is decomposed by hot, strong hydrochloric acid, and is dissolved by hot concentrated sulphuric acid and many salt solutions, *e.g.* ammonium acetate, sodium thiosulphate, etc.

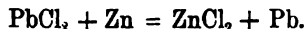
5. Sodium hydrate precipitates white lead hydrate, $Pb(HO)_2$, soluble in excess.

6. Ammonia produces the same precipitate insoluble in excess of the reagent.

7. Sodium carbonate precipitates white lead carbonate insoluble in excess, soluble in acetic acid.

8. Sulphuretted hydrogen produces a black precipitate of lead sulphide, PbS , which is soluble in dilute nitric acid, but is converted into white lead sulphate by strong nitric acid. Filter off the precipitate before testing its solubility.

9. Zinc added to a solution of any lead compound precipitates the lead, as metal—



Treatment of Insoluble Substances.—Fuse with fusion mixture, and boil the fused mass with water. Filter. Dissolve the residue in weak nitric acid, and test as above.

Substances suspected to contain galena may be dealt with as follows: Put a little of the fine powder in an evaporating dish, add a little strong nitric acid, and warm till all action ceases (red fumes are no longer evolved). Evaporate to dryness. Take up with a little dilute sulphuric acid, filter, and wash. This treatment converts the lead sulphide into sulphate which is soluble in ammonium acetate. Wash the residue off the filter into a beaker with dilute ammonia, warm and acidify with acetic acid, boil, filter, and test filtrate with potassium chromate.

Or they may be treated with strong hydrochloric acid and zinc as directed on p. 64.

DRY ASSAY OF LEAD ORES.

In the dry assay of sulphurized materials, iron is used as a desulphurizing agent, but an addition of argol or black flux is generally made to effect the reduction of any carbonate or sulphate (to sulphide) that may be present. It also prevents the oxidation of the iron sulphide

formed. Iron oxides, especially in iron crucibles, have a tendency to cause the retention of lead in shots on the sides of the pot. The reduced lead contains the greater part of the antimony and a small portion of the copper, but very little of the iron or zinc in the ore. All the silver and gold pass into the lead if the button be sufficiently large. Of the arsenic present a portion may be volatilized, but the greater part combines with iron and produces speiss.

When barytes (heavy spar) or bone ash, phosphate of lime, have to be fluxed, an addition of fluor spar is made for that purpose.

Oxidized compounds are reduced by carbon or carbonaceous bodies.

Materials of Class I.—In an Iron Crucible. Finely powder the material and pass through a 60 sieve.

Weigh out—

25	grms.	or	400	grs.	ore.
25	"	"	400	"	carbonate of soda.
2	"	"	30	"	argol.

Thoroughly mix, and put the whole in the copper scoop. Put about 5 grms., or 75 grs. of borax behind the assay mixture. When the pot is at a dull cherry red heat, shoot the contents of the scoop into it so that the borax forms a cover. A salt cover is sometimes used. Heat to full redness till quietly fused. Push down any matter clinging to the sides with an iron rod. Remove from fire, tap gently, and pour. Examine the crucible for shots of lead. If any are found, put some sodium carbonate and a little argol into the crucible and run down again.

Thoroughly clean the button (by hammering on the edges and brushing), and weigh. The result, multiplied by 4, if gram weights are used, or divided by 4 if grains, gives the percentage of lead. Examine the slag. If it contain shots it must be remelted with potassium carbonate. This method is suitable for all galenas.

In a Clay Pot.—The mixture is made as before, and iron nails or pieces of hoop-iron are used to desulphurize. Three 3-inch wire nails pushed down into the mixture answer well or a strip of hoop-iron $\frac{1}{2}$ inch wide and 5 inches long bent U-shaped is placed in the pot and the mixture filled in round it, the borax as before being used as a cover. When fusion is complete (from 20 to 25 mins.), the nails are tapped on the side of the pot, removed separately, each being washed in the slag to detach any adherent lead. The bent strip is dealt with in the same way. The crucible is taken out, tapped, and poured as before.

The loss of lead in dry assay varies. It generally amounts to from 0.5 to 6 %, but is dependent on the temperature and the length

of time occupied. The temperature necessary to produce complete fusion should not be exceeded, and when attained should not be prolonged. Pure galenas containing 86.6 % lead yield from 84 to 85.25 of lead. With from 10 to 30 % calcium carbonate the loss ranges from 1.8 to 7.9 %. With the same amounts of silica from 1.18 to 35 % (Percy). In an iron pot the operation after introducing the mixture should occupy about 10 to 13 mins., divided as follows:—4 to 5 mins. heating up charge, 4 to 5 mins. steady heat, and a final heating with the furnace closed for two or three minutes. In a clay pot a longer time is required to heat the charge.

Lead mattes, slags, etc., may be dealt with by this method. For poorer ores less sodium carbonate and more borax are employed. 25 grms. or 400 grs. ore, 20 grms. or 320 grs. of soda, and 10 grms. or 160 grs. of borax. Galenas with large quantities of silica are assayed as follows: 100 grms. ore, 150 grms. sodium carbonate, 150 grms. potassium carbonate, an iron strip, and 10 grms. borax as a cover. The time of fusion may occupy from $\frac{1}{4}$ to $1\frac{1}{2}$ hour. The iron must be free from lead globules.

Class II.—Assay of Oxidized Materials. Assay of Lead carbonate, Pyromorphite, etc.

25 grms. or 400 grs.	ore.
25 " " 400 "	sodium carbonate.
6 " " 100 "	argol.
3 " " 50 "	borax.

The ore finely powdered and sieved, should be thoroughly mixed in a mortar, transferred to a "lead assay" crucible, heated gradually till the mixture is fused (15 to 20 mins.), and kept fused at full redness for about 10 mins. Remove from fire, tap gently, and pour into a mould. Clean the lead button, and weigh. If any sulphide be present, a strip of iron should be added.

Pyromorphite, chromate of lead, wulfenite, and mimetesite (arsenate of lead) may be assayed by this method, but with the addition of 50 % more carbonate and a little—0.5 to 1 grm. of lampblack. With the arsenate a thin strip of iron should be added.

Assay of Red Lead.

25.0 grms. or 400 grs.	ore.
25.0 " " 400 "	carbonate of soda.
1.5 " " 25 "	lampblack.
3.0 " " 50 "	borax.

Assay of Cupel Bottoms.

25.0 grms. or 400 grs.	cupel.
25.0 " " 400 "	carbonate soda.
6.5 " " 100 "	fluor spar.
8.0 " " 150 "	borax.
2.0 " " 30 "	lampblack.
or, 12.5 " " 200 "	argol.

Fuse for about 15 mins. and pour. Clean the button, and weigh. If 25 grms. of borax be employed, the fluor spar may be omitted, but the tendency of the assay to boil over is greatly increased.

Ores containing barytes may be treated in the ordinary manner with an addition of fluor spar equal in weight to the barytes present.

Lead slags.—Slags containing sulphide or silicate are dealt with in the same way as poor galenas (see *ante*). In treating slags the time occupied is longer than for ores.

WET METHODS OF ESTIMATION.

Methods of Solution.—Substances of the first class occasion some little difficulty, for although lead sulphide is soluble in dilute nitric acid, with fairly strong acid it is to a large extent converted into an insoluble sulphate, and with very strong acid may be completely so converted. In this form it may be separated and afterwards estimated.

When heated in a finely divided state with strong hydrochloric acid and zinc, the sulphide, though not readily soluble in the acid, is decomposed freely. Sulphuretted hydrogen is evolved and lead chloride formed. This is immediately decomposed by the zinc, which precipitates the metal in a spongy form. In this condition it may be removed from the liquid, dissolved in nitric acid, and estimated.

Oxidized compounds give little trouble. The lead is readily soluble in dilute nitric acid. Silicates and slags require fusing with sodium and potassium carbonates. The mass is then extracted with water and washed, and the residue which contains the lead dissolved in nitric acid.

Preparation of Solutions from Substances of Class I.—Weigh out the required amount of material in as fine a state of division as possible.

Method I.—Cover the substance with dilute hydrochloric acid, and heat gently to about 70° C. Add a weighed rod of pure zinc. (The zinc should be previously tested for lead, and the amount it contains, if any, estimated.) Continue heating till solution is complete, and only a sponge of lead and the insoluble impurities remain. By means of a glass rod detach the lead from the zinc. If the zinc contains lead,

weigh the remainder and calculate the amount of lead added to the assay by the zinc dissolved. This must be deducted from that found. Dilute with water, filter and wash. Dissolve the precipitated lead in nitric acid (1 part acid, 2 parts water). Filter off any insoluble matter. The solution contains the lead as nitrate. This method of treatment answers for sulphides and most lead ores, including sulphates, if the time of solution be prolonged.

Method II.—Place the finely powdered ore in an evaporating dish, cover with moderately strong nitric acid, and heat gently. When action ceases, dilute to 100 c.c. for each grm. of galena or its equivalent present, add 10 c.c. of dilute sulphuric acid (1 in 4), and evaporate nearly to dryness (till fumes of sulphuric acid are given off). The insoluble residue contains the lead as sulphate. After cooling, dilute with water to 100 c.c., filter, and wash twice with water acidulated with sulphuric acid, and finally once with water. Wash down the precipitate into a beaker, or place the paper and its contents in a beaker, with 5 c.c. to 10 c.c. strong ammonia, acidify with acetic acid, and boil. Filter and wash with weak ammonium acetate. The lead is in solution as sulphate.

NOTE.—Lead sulphate is soluble in ammonia acetate. Sodium acetate may also be used as a solvent, caustic soda followed by acetic acid being employed.

Method III.—Instead of ammonium or sodium acetates, a warm saturated solution of sodium thiosulphate ("hypo") may be employed for solution. The filtered residue after thorough washing is treated three or four times with the solution, a short interval being allowed between each treatment. The solution may be saturated with sulphuretted hydrogen when the lead is precipitated as sulphide, and may be dealt with as in Method I. For very impure ores, Methods II. and III., though more complicated, are to be preferred to Method I.

Preparation of Solutions for Substances of Class II.—These are best treated by Method I., given above, but pure carbonates, litharge, etc., may be dissolved at once in dilute nitric acid. Slags require fusion with four times their weight of carbonates of soda and potash in a platinum crucible. The melted mass is boiled with water and filtered, the residue being dissolved in weak nitric acid or dealt with by Method I. Great care is necessary to exclude reducing agents during the fusion, or lead may be reduced and the crucible injured. Shots of lead must be removed before fusion.

Substances of Class III. are dissolved in nitric acid, and evaporated to small bulk.

GRAVIMETRIC DETERMINATION.

Estimation as Lead Sulphate.—Sulphate of lead is almost insoluble in water, and still less soluble in dilute sulphuric acid and insoluble in alcohol. It is sensibly soluble in nitric acid, and is not fully precipitated in the presence of the free acid and some of its salts. It is also soluble in hot concentrated sulphuric acid. The sulphate is decomposed and dissolved by boiling concentrated hydrochloric acid.

In view of these facts, careful treatment is necessary. The solution prepared by any of the above methods is evaporated with sulphuric acid till the fumes of the acid are given off. The solution is diluted with water, allowed to settle, filtered, washed by decantation with water acidulated with sulphuric acid, and finally on the filter with dilute alcohol or water. Care must be taken to remove all the acid, or on drying the paper will char. (Test the last drop of the washings with barium chloride.) Dry the precipitate, and remove it as completely as possible from the paper. Burn the paper, and treat the ash on the inverted crucible lid with a drop or two of nitric acid, and warm, then add a drop of sulphuric acid, and heat gently till all the acid is expelled. Put the cover on the crucible, and ignite gently. Let cool and weigh (see p. 32). Factor for lead = 0.68295.

Estimation of Lead in Galena.—Weigh out 1 grm. of galena in a deep evaporating dish. Cover with 20 c.c. strong hydrochloric acid and 40 c.c. water. Warm till action ceases, then add a rod of pure zinc, and keep warm. The decomposition will be complete in about 20 mins., and is apparent when sulphuretted hydrogen is no longer evolved. Fill up the dish with warm water, and decant through a filter. Repeat as quickly as possible three or four times till the washings are free from acid. Then detach the lead sponge from the zinc with a glass rod or policeman. Rinse the zinc over the filter. Wash any flakes of lead on the filter back into the dish. Treat the residue with 10 c.c. dilute nitric acid (1 : 1) till the lead is dissolved; dilute to 50 c.c., filter off the gangue, and wash. To the filtrate, add 10 c.c. dilute sulphuric acid (1 : 1). Evaporate till it fumes, dilute with water, let settle, filter, and wash first by decantation with acidulated water, then on the filter with water and alcohol. Dry, ignite, as directed above, and weigh the precipitate.

Factor for lead = 0.68295, and if 1 grm. be taken % = weight of lead found obtained $\times 100$.

This method is almost universally applicable. Sulphate, chromate, chloride, nitrate, oxides, carbonate, and phosphate, all yield to this treatment. Silicates require fusion and treatment as described (p. 63).

Estimation of Lead as Carbonate.—The solution of lead nitrate prepared by Method I. is treated with a solution of ammonium carbonate mixed with ammonia. For this purpose one-third of its volume of strong ammonia is added, then a 10 per cent. solution of ammonium carbonate in excess. The solution is gently warmed, and let stand 12 to 24 hours. The precipitate is collected in double counter-poised filters (p. 52), washed with warm water, dried at 100° to 110° C., and weighed. This method is not accurate to more than 0.25 per cent. Factor for lead = 0.77503.

VOLUMETRIC METHODS OF ESTIMATION.

Method I.—Estimation by Standard Potassium Chromate.—This method yields good results under certain conditions.

1. The solution must contain no free acid, or, only a trace of acetic acid.
2. It must be titrated boiling, or the precipitate settles slowly.
3. The precipitate being slightly soluble in acetates, excess must be avoided.
4. Sulphates must be absent.
5. The temperature and volume of the solution must be uniform.

For the conducting of many determinations at one time the method is fairly quick and reliable.

Standard Bichromate Solution.—Dissolve 7.36 grms. of the salt in water, and dilute to a litre. 1 c.c. of this solution = 0.00103 gm. lead.

Sodium Acetate Solution.—Dissolve 100 grms. in 1 litre of water. Use 50 c.c. = 5 grms. sodium acetate for each assay. The salt may be added solid if preferred.

Standard Lead Solution for titrating back.—Dissolve 16.5 grms. of recrystallized lead nitrate in a litre of water. 1 c.c. = 0.00103 gm. lead.

Silver Nitrate Solution.—Five grms. of the salt are dissolved in 100 c.c. distilled water.

Standardizing.—Take 50 c.c. of the lead nitrate solution. Test for neutrality, add 50 c.c. sodium acetate solution, and titrate hot. Run in nearly the required amount (50 c.c.) of bichromate solution. Stir well, and test a drop of the solution on a spot plate with a drop of silver nitrate. Continue the titration carefully till, on testing with silver nitrate, a red colour (silver chromate) is produced. For ordinary work, a sufficient degree of accuracy may be obtained in this way, but

for very accurate work 2 c.c. of the lead solution is added and the titration continued, the solution being added drop by drop as the end is approached. This is easily calculated, as the standard lead and standard bichromate solutions are of equivalent strengths. The liquid should not assume a yellow colour till the end of the reaction. If it does, too much free acetic acid is present. This may be remedied by adding more sodium acetate, but not more than 10 grms. should be present. If too much bichromate be used, a measured quantity of the lead nitrate solution may be added and the titration continued. The lead added during the assay must be taken into account in making calculations. Calculate the amount of lead to which each c.c. of the bichromate solution is equivalent.

Determination of Lead in Ores.—Take 1 grm. of the ore, and prepare the solution as directed (pp. 62, 63). Dilute the solution to 100 c.c. Add a very slight excess of sodium carbonate solution, heat to boiling, dissolve the precipitate in the minimum quantity of acetic acid (only a mere trace of free acid should be present), add 50 c.c. of sodium acetate solution, and titrate hot. Stir vigorously while running in the solution, and near the end the precipitate should be allowed to settle before withdrawing the drop for the test plate. Determine the end of the reaction with silver nitrate, as in standardizing.

Note the volume of solution taken. This multiplied by the standard as determined above gives the quantity of lead in the solution.

Method II.—Estimation of Lead by a Standard Solution of Ammonium Molybdate. *Alexander's method.**—Lead molybdate is insoluble in water and acetic acid. Precipitated in hot solutions by the addition of ammonium molybdate it settles quickly, and the addition of an excess of the reagent may be rendered apparent by means of tannin on a spot plate, as ammonium molybdate gives a brownish-yellow colour with freshly prepared solutions of tannin.

Standard Ammonium Molybdate Solution.—This is prepared by dissolving 10 grms. of the finely-powdered salt (not white on the outside) in water. A little ammonia is added, if necessary, to clear the solution, which is then diluted to a litre.

Tannin Solution.—This must be freshly prepared by dissolving 0.1 grm. of tannin in 30 c.c. of water.

Solution of Lead Sulphate for Standardizing.—3 grms. of lead sulphate (freshly prepared by preference) is dissolved in hot ammonium acetate solution. This is done by weighing out 3.211 grms. of lead nitrate, and converting it into sulphate by evaporation with sulphuric acid. If not freshly prepared, the salt may be ground up

* *Engineering and Mining Journal*, April 1, 1893.

with the solid ammonium acetate, in a mortar, and dissolved. The solution is diluted to a litre. Each c.c. contains 0.003 grm. of PbSO_4 , and is equivalent to 0.0020488 Pb. 100 c.c. of this solution is diluted to about 250, acidified with acetic acid heated to boiling, and titrated with the ammonium molybdate solution. The liquid must be thoroughly shaken or stirred after each addition of molybdate. After settling, drops are removed by a glass rod and brought into contact with drops of the indicator on a spot plate, the addition of molybdate being continued till a faint yellow colour is obtained. Care must be taken to keep the liquid hot. The lead value of the standard ammonium molybdate solution is then calculated.

The Assay.—The lead is first obtained as sulphate by any of the ordinary methods of procedure. Galenas may be directly oxidized by strong nitric acid and a little sulphuric acid. The sulphate, after careful washing, is dissolved by digestion in a hot concentrated solution of ammonium acetate (see Method II. p. 63), acidified with acetic acid, heated to boiling, and titrated as nearly boiling as possible, in the same manner as for standardizing.

COPPER.

SUBSTANCES IN WHICH THE METAL HAS TO BE DETERMINED

1. ORES and furnace products.

- (A) Substances containing the copper as oxide, with or without the presence of metallic copper.
- (B) Substances containing the copper as sulphide.
- (C) Sulphantimonides and sulpharsenides.

2. Copper precipitate ; crude copper ; metallic alloys.

Copper Ores.—*Class A.* Yield copper when heated on charcoal before blowpipe with fusion mixture. With borax in the oxidizing flame they yield a blue bead (greenish while hot), and in the reducing flame a red opaque bead.

Cuprite, Red Copper, Cuprous oxide, Cu_2O , is a crystalline mineral, dark to bright red, with a bright red streak. It also occurs massive. It dissolves in nitric acid, and becomes permanently black when heated in an open tube, Fig. 81 ($\text{Cu}_2\text{O} + \text{O} = 2\text{CuO}$), distinction from red hematite, cinnabar, and zinc oxide. Sp. gr., 5.7—6. Hardness, 3.5—4.

Tenorite, Malaconite, Cupric oxide, CuO , is an earthy black mineral, generally occurring as an incrustation, and associated with other ores. Gives green solution with nitric acid (distinction from cobalt and manganese oxides).

Malachite, $\text{CuCO}_3\text{CuH}_2\text{O}_2$, basic carbonate of copper, is a green mineral, often banded in different shades of green, and with a silky lustre. Gives reactions as above. Blue bead with borax distinguishes it from nickel ores (garnierite), and green solution with nitric acid from green lead ore. Occurs associated with other ores of copper. Sp. gr., 3.6—4. Hardness, 3.5—4.

Azurite, Chessylite, $2\text{CuCO}_3\text{CuH}_2\text{O}_2$, is a blue mineral, occurring well crystallized, and in massive and earthy forms. Gives the same reactions as malachite. Sp. gr., 3.7—3.8. Hardness, 3.5—4.

Chrysocolla, $\text{CuO}, \text{SiO}_2, 2\text{H}_2\text{O}$, is a blue hydrated silicate of copper, giving a white streak. It is soft and light. Sp. gr., 2—2.3. Hardness, 2—3.

Diopside, $\text{CuOSiO}_3 \cdot \text{H}_2\text{O}$, is a green vitreous mineral. Sp. gr., 3.27. Hardness, 5.

Atacamite, $\text{CuCl}_2 \cdot 3\text{CuO} \cdot \text{H}_2\text{O}$, is a green mineral often crystallized. If heated in Bunsen flame, tinges it blue round the fragment and green above.

Class B.

Redruthite, Copper Glance, Cu_2S , cuprous sulphide. Fresh fractures have a lead or iron-grey colour, and a sub-metallic lustre which tarnishes bluish black. It is soft enough to be cut with a knife, brittle, and heavy. Sp. gr., 5.5—5.8. Hardness, 2.5—3. The streak is grey and shining.

Erubescite, Bornite, Horse-flesh ore, $3\text{Cu}_2\text{SFeS}_2$ (composition variable), is a very brittle mineral, with a reddish bronze colour, and high lustre on freshly fractured surfaces, but tarnishes a peacock blue, with other tints. Sp. gr., 4.9—5.1. Hardness, 3.

Copper Pyrites, Yellow Copper Ore, Cu_2SFeS_2 or CuFeS_2 , has a golden yellow colour, a metallic lustre, is soft enough to be scratched with a knife, and is brittle. It is the commonest and most important ore of copper. Sp. gr., 4.1—4.3. Hardness, 3.5—4.

Class c. Containing other metals than copper and iron.

Grey Copper Ore, Tetrahedrite, Fahl Ore, $4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$, is a brittle mineral, with a steel grey fracture and metallic lustre. Its composition is very variable, the antimony being replaced by arsenic, and occasionally by bismuth, and the copper replaced by iron, lead, silver, gold, mercury, and zinc. It is often argentiferous. The antimonial varieties give a reddish sublimate of sulphide of antimony when strongly heated in a closed tube. It contains up to 26 per cent. of copper. Sp. gr., 4.5—5.2. Hardness, 3—4.

Bourbonite, $4\text{PbS} \cdot \text{Sb}_2\text{S}_3 + 2\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$, is a very brittle mineral, often well crystallized, with a brilliant metallic lustre. It is lead grey in colour, and soft. It contains from 10 to 15 per cent. of copper. Sp. gr., 5.7—5.9. Hardness, 2.5—3.

Libethenite and phosphorhalcite are green phosphates of copper, and olivenite and liroconite are arsenates of copper.

Furnace Products.—*Class A.* **Slags**, clean slag, metal slag, roaster and refinery slags, consisting of silicates of iron and copper, of greater or less richness, and sometimes containing metallic copper.

Class B. **Mattes and reguli**, consisting of copper and iron sulphides. Coarse, white, purple, bronze, fine metal, etc.

Metallic Products.—Copper precipitate, Chili bar, native copper concentrates, blister copper, bottoms, etc.

CHEMICAL REACTIONS FOR COPPER.

Dry Reactions.—Copper is fusible before blowpipe, and becomes covered with black oxide in an oxidizing flame.

(a) Substances of first-class (oxidized bodies), mixed with fusion mixture (see p. 37), yield metallic copper when heated in the reducing flame before the blowpipe.

(b) Substances containing sulphur or arsenic require roasting in an oxidizing flame to remove those elements before heating with fusion mixture. This may be done before the blowpipe on a little iron spoon (Fig. 60) or a plaster plate.



FIG. 60.

(c) Substances of both classes give, after roasting, a blue bead with borax in the oxidizing flame, and a red opaque bead in reducing flame.

(d) Bodies containing copper when moistened with hydrochloric acid, and heated on platinum wire in the lower part of the Bunsen flame, give a blue colour (copper chloride) in the vicinity of the wire and green above. Sulphurized bodies require roasting before applying this test.

Wet Reactions for Copper.—The metal dissolves readily in nitric acid, $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$. In sulphuric acid sulphur dioxide is liberated on heating, but the solution of the copper is not complete owing to the formation of sulphide by reduction of the sulphate. Hydrochloric acid does not dissolve copper except in the presence of oxidizing agents, but the metal is soluble in aqua regia.

Solutions of cupric salts are blue or green.

1. Sulphuretted hydrogen in acid or alkaline solutions throws down a brownish black precipitate of cupric sulphide (CuS), which is soluble in hot nitric acid (with separation of sulphur) and in potassium cyanide.

2. Sodium thiosulphate added to a slightly acid solution decolourises it, and on boiling cuprous sulphide (Cu_2S) is precipitated.

3. Ammonia throws down a bluish white precipitate which dissolves in excess, giving a dark blue solution. Ammonium carbonate behaves similarly. The colour is discharged by potassium cyanide.

4. Sodium hydrate throws down a bluish precipitate, which, on heating to boiling, turns black. In presence of tartaric acid, Rochelle salt, and many organic salts, no precipitate is produced, but a blue solution, from which grape sugar and other reducing agents, on warming, throw down red cuprous oxide.

5. Potassium iodide throws down a creamy precipitate of cuprous

NOTE.—Ferrous sulphate, or other oxidizable substance, prevents the separation of iodine; thus: $2\text{CuSO}_4 + 2\text{FeSO}_4 + 2\text{KI} = \text{Cu}_2\text{I}_2 + \text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4$.

iodide, and the solution becomes brown, iodine being liberated at the same time. $\text{CuSO}_4 + 4\text{KI} = \text{Cu}_2\text{I}_2 + \text{K}_2\text{SO}_4 + 2\text{I}$.

6. Zinc or iron throws down copper at once from acid solutions.

7. Ferrocyanide of potassium throws down a deep chocolate-coloured precipitate of copper ferrocyanide ($\text{Cu}_2\text{FeC}_6\text{N}_6$).

8. Sodium carbonate produces a green precipitate soluble in ammonia and in acids.

DRY ASSAY OF COPPER.

Cornish Assay.—This method, though only approximately accurate, is largely followed, and in skilled hands yields good results. It has many things to recommend it. It can be completed more quickly than a wet assay, and a button of copper is obtained, the refining of which gives some clue to the character of the copper which will be obtained on smelting. As a means of estimating the amount of copper actually present, it is, however, unsatisfactory. The result is always below the actual copper contents, the deficiency depending on the richness of the material treated, and the nature of the foreign constituents present.

Below is given a table of the approximate loss in dealing with ores of different grades—

Copper present in 100 parts.	Found by dry tests.	Loss.	Percentage loss in terms of copper.
100	98.5	1.5	1.5
95	92.5	2.5	2.6
75	72.4	2.6	3.5
55	52.7	2.3	4.2
35	33.25	1.75	5.0
25	23.5	1.5	6.0
15	13.51	1.5	10.0
10	8.72	1.28	12.8
5	4.0	1.0	20.0
4	3.0	1.0	25.0
3	2.125	0.875	29.0
2	1.333	0.66	33.0

The dry assay of copper follows more or less closely the methods employed in copper smelting, and is based on the facts that copper has a greater affinity for sulphur and a less affinity for oxygen than iron, tin, lead, bismuth, antimony, zinc, or arsenic. By alternate roasting and fusion the copper is concentrated in a rich regulus, from which it is separated and subsequently refined.

The process involves six or seven operations, according to the method followed and the richness and character of the ore. Since the copper cannot be advantageously separated from a regulus containing less than 50 per cent. of copper the preliminary stages are devoted to its concentration to at least that extent, and the number of processes

necessary depends on the readiness with which this degree of concentration can be obtained.

Copper ores containing the copper in the form of carbonate or oxide are treated in a special manner (see p. 77).

Assay of Sulphurous Materials, including pyrites, erubescite, peacock ore, bournonite, tetrahedrite, and mattes.

Summary of Operations.—

- | | | |
|--|---|---|
| <p>I. Roasting of material to partially remove sulphur, and convert iron and copper into oxides.</p> <p>II. Fusion with fluxes to remove oxide of iron and gangue and produce regulus.</p> | } | <p><i>Or, fusion with oxidizing agents and fluxes to produce a regulus.</i></p> |
|--|---|---|

III. Roasting regulus, "sweet," *i.e.* free from sulphur.

IV. Fusion with reducing agents to obtain coarse copper.

V. and VI. Washing and refining the coarse copper.

VII. Reducing slags for prill.

Ores are worked through all stages. Mattes, if over 40 per cent., are not run for regulus. Copper precipitate is melted at once for coarse copper, and refined, unless it contains metallic iron. Blister copper is refined.

I. *Preliminary Roasting.*—The ore is passed through a 40-mesh sieve, and 400 grms. or 25 grms. is weighed. If rich, only half this quantity is taken. The ore is put into a large Cornish "copper assay" crucible, and if poor, very carefully roasted to expel excess of sulphur. The fire is made up and the pot placed on the top, the bottom of the crucible only being slightly embedded. It is allowed to attain very dull redness, being stirred continuously with a flattened iron rod. The roasting is complete when, on lifting the crucible by the tongs and inclining it from side to side, the powdered ore falls freely about like red-hot sand. Care must be taken not to heat too strongly, or the material may clot, and not to over roast, as a slightly under-roasted charge is preferable to an over-roasted one.

II. The charge is then mixed with—*

1 ladleful,	or 20 grms. of lime.
„ 15	„ glass.
„ 15	„ fluor spar.
„ 10	„ borax.

NOTE.—This ladle is roughly 1½ in. diameter, and slightly concave. A teaspoon may be substituted.

* Redruthite and grey copper ores will also require an addition of from 5 to 15 grms. of a mixture of 1 part red hematite, 2 parts sulphur, 2 parts argol, or 1 part tartar, 2 parts sulphur, to collect the copper.

These are added in the pot and the whole stirred well together with a spatula or a stirrer, and covered with salt. The crucible is then covered with a lid, and slowly and uniformly heated up to very bright redness. For this purpose the pot must be well surrounded by the fire, but care taken that coke does not get into it, otherwise iron may be reduced and separate some copper. When quite fluid, the contents are poured, and as soon as the slag is solidified, the button is seized with the small tongs and dipped in water a few times, waiting a few moments between each dip. A convenient handle for holding the button while dipping it is formed by pinching up the top of the slag button before it solidifies. This method of quenching causes the slag to crack, and on cooling and gently tapping with a hammer it detaches itself completely from the button. As the regulus is extremely brittle, it is essential that the slag should not require hammering to separate it. If difficulty is encountered the slag must be remelted.*

The button should be well rounded above, clean looking, and have a bronzy brownish red to bluish colour. It should contain from 40 to 70 per cent. of copper. If the copper exceeds 70 per cent. the button will be whitish and metallic, round, compact, and hard. If it be too poor (coarse) it will be very dull and granular, flat, and irregular. The fracture should be moderately fine grained. If the regulus is not satisfactory, a fresh beginning should be made, giving less or more roasting as required. The charge should be very fluid before pouring.

III. Roasting the Regulus.—The regulus is carefully detached from the slag, ground in an iron or bronze mortar,† and placed in a seconds crucible (or on a roasting dish, if the roasting is to be done in a muffle). The crucible is placed on the top of the fire which was made up on withdrawing the pots after fusing the ore, and sloped forward. It is carefully roasted with constant stirring at a dull red heat, ultimately attaining full redness. As the roasting proceeds, there is less liability to clot, and the ore becomes sandy. When no further smell of sulphur dioxide is perceived, a pinch of ground anthracite or charcoal is added, well mixed in the mortar if necessary, *i.e.* if the charge has clotted, and the roasting continued till the anthracite has burnt off. This reduces any sulphate that may have been formed during the roasting, and allows the sulphur that would otherwise be retained to oxidize. The iron and copper are now present as oxides. No smell of sulphur dioxide must be perceptible when the crucible is withdrawn from the fire, and

* Slags may be cleansed by remelting with the addition of a little finely powdered iron pyrites free from copper, or with the mixture given in footnote on previous page.

† The mortar is carefully cleaned by grinding a few grains of anthracite in it and adding this to the charge.

the product must contain no lumps. Any sulphur retained interferes in subsequent stages, by forming a coat of regulus over the button.

IV. Fusion for Coarse Copper.—The roasted regulus is mixed in the pot with—

2 ladles or	20 grms. of white tartar.
2 „ or	20 „ sodium carbonate.
$\frac{1}{4}$ to $\frac{1}{2}$ „ or 2·5 to 5	„ nitre.
$\frac{1}{2}$ „ or	5 „ borax.

The substances are stirred together with a spatula, and a cover of salt put on. The pot is then transferred to the furnace, well coked up, and carefully heated to complete fusion, care being taken to so manage the heating that the contents do not boil over. When in a state of quiet fusion, a little refining flux (see p. 75) is added. This makes the contents of the pot boil, and washes down any small prills of copper adhering to the sides of the pot. The temperature is raised to the highest point, and kept at that for a few minutes, taking care that the crucible is hot to the top. The pot is then withdrawn, gently tapped on the bottom, and the contents poured quickly but steadily into a mould. Success depends largely on fluidity, and this on the temperature.

The button of copper is broken out and examined. If clean and coppery looking (not black and shiny), the washing may be omitted.

V. Washing.—When the button is black and dirty looking, it is thrown back into the hot crucible, and enough of a mixture of refining flux (1 part) and salt (2 parts) added to cover it. The charge is kept fluid for some time, and poured. The button should now be clean.

The slags from the running for coarse copper should not be red. If they are, too little tartar has been used, or too much nitre. They must be preserved, and also the slags from subsequent operations.

VI. Refining the Copper.—The pot in which the fusion was effected is placed in the furnace, and heated nearly to whiteness.* Meanwhile half a ladleful of refining flux is placed in the front of the copper scoop, and enough salt to cover the button behind it. Drop the button of copper into the pot, and when melted and fully hot, lift the pot with the tongs in the right hand, having the scoop in the left. Gently move the right hand so as to make the copper run about the bottom of the pot, and watch closely. Films of oxide make their appearance rapidly at first, but by moving the pot they clear. Keep moving till no further film forms and the “eye” is clear copper. Instantly shoot the contents

* If for any reason a new pot is employed, it must be glazed with borax before use.

of the scoop into the pot, and replace in the furnace. A moment's delay in adding the flux may spoil the assay. The pot is heated as strongly and rapidly as possible, the assay poured, and the pot returned to the fire. The button on breaking out should have a fine colour, and a flat surface or a little pit in the centre, and it may have a yellowish tinge. If purple on the surface it is burnt. If rough and dull it is not sufficiently fine, and must be returned to the pot and again refined. The button must be tested by nicking and bending over in the vice. It should be strong and tough.

VII. **Fusion of Slags for Prill.**—The slags from the 4th, 5th, and 6th operations are rubbed down in a mortar, mixed with a teaspoonful of argol, a little sodium carbonate, and a few grains of charcoal, fused at a high temperature and poured. The little prill of copper is separated, and if large enough refined. The resulting slag should be black and free from red streaks.

Refining Flux.

3	parts by measure	white tartar.
2	„ „	nitre.
1	„ „	borax.
1	„ „	salt.

These are mixed, and kept in an air-tight vessel. Most assayers only mix enough for the assays in hand. If the copper is very impure, a sharper, *i.e.* a more oxidizing, flux may be employed—

2½	parts	white tartar.
3	„	nitre.
1	„	salt.
½	„	borax.

Success can only be attained by good furnace management. The fusion for regulus will occupy 20 to 25 mins.; roasting of regulus about 30 to 45 mins.; fusion for coarse copper, 12 to 15 mins.; washing, 5 to 6 mins.; refining, 3 to 5 mins. These times only refer to the time the charge is actually in the furnace, and may be much prolonged.

The instructions here given for the dry assay of copper must be taken as general. Slight modifications will be necessary in many cases. More or less flux will be required according to the nature of the materials treated, and other changes may be made.

A note of the action of the various reagents in different parts of the process may be serviceable as a guide.

Fluor spar is employed in the preliminary fusion, not to serve as a flux for silica, but to render the slag brittle and easily detached by

quenching. It combines with silicate of lime, and forms a readily fusible fluo-silicate.

Carbonate of soda, where used, acts as a flux for silica, and is also to some extent a desulphurizing agent.

Nitre is used as a desulphurizing and oxidizing agent. It aids in securing the passage of the easily oxidizable metals into the slags.

Salt is used as a cover to prevent boiling over. In the earlier stages of the assay it is also used to render slags fluid, while in the washing and refining stages it is employed to effect removal of antimony and arsenic as volatile chlorides. As copper chloride is also volatile, it may cause the loss of some copper.

Argol is employed as a reducing agent, and also acts as a desulphurizer. The amount used should be regulated by the weight of the regulus button and the amount of copper it contains. Excess will reduce foreign metals, and make the copper very coarse. These remarks apply both to the reduction of roasted regulus and refining. The less pure the regulus, the less tartar. Impure copper, less tartar, relatively more nitre, and thus a sharper flux.

Yellow Copper Ores may be fused for regulus direct, with nitre in addition to the other fluxes. Take—

25 grms.	ore.
20 „	lime (slaked powder).
20 „	fluor.
15 „	glass.
5-10 „	borax.
5-10 „	nitre.

The regulus, after roasting, may be melted with—

10 grms.	argol.
20 „	carbonate of soda.
2-3 „	borax, under a salt cover.

If the slag is red, grind and mix it with 5 grms. argol and a little soda, and remelt before proceeding. Add the copper obtained to the other button. Wash the button with refining flux and salt. Test by flattening on anvil, wrapped up to prevent loss. Grey brittle copper may contain antimony, but iron and other elements may produce the same result. Wash under salt again, if necessary. Lastly refine. Treat the slags for prill as before.

In dealing with pure sulphides, sulphide of iron is often introduced in the preliminary fusion in the form of iron pyrites, in order to produce a regulus which more nearly corresponds to the character of the regulus generally obtained.

Dry Assay of Copper.—German Method.—1. The ore is roasted with addition of ammonium carbonate.

2. Heated with metallic arsenic.
3. Fused with fluxes to collect speiss, consisting of arsenides of copper, iron, cobalt, and nickel.
4. Scorified to remove iron and cobalt.
5. Scorified with gold to remove nickel. See Dry Assay of Nickel and Cobalt.

Dry Assay by Fusion with Potassium Cyanide.—This method is only applicable to pure ores and mattes free from antimony, bismuth, zinc, lead, tin, etc., for which purpose it is especially useful.

Ten grammes of ore or matte are roasted, solid ammonium carbonate added, and finally a little charcoal. The roasted material is mixed with 30 grms. of KCN and 5 grms. of borax, and covered with other 10 grms. of KCN. A cover of salt (15 grms.) is put on, and the whole fused for about 30 mins. in a hot fire. If the substance contains little or no iron, about 2 grms. of red hæmatite must be added to prevent copper being carried into the slag by the borax, etc.

The button may be refined in the usual way.

Assay of Oxidized Copper Ores.—Oxides and Carbonates.—Powder and sift the ore. Weigh out—

10 to 20 grms. ore.
2 „ 4 „ charcoal.
or 12 „ 24 „ argol.
10 „ 20 „ sodium carbonate.

Or 20 grms. ore, 15 grms. argol, 15 grms. sodium carbonate, 10 grms. borax.

Mix thoroughly, transfer to a copper assay crucible (small or large seconds) and heat strongly for 20 mins. Then add 5 grms. borax and a little argol, and heat strongly till slags are quite fluid. Before pouring add a pinch of refining flux (see p. 75), and when quietly fused pour into a mould. If borax be mixed with the assay at first, there is a tendency for the slag to fuse too readily. This causes oxide of copper to pass into the slag, which becomes blue or red. It is extremely difficult to reduce the copper from the fluid slag. By the above procedure this difficulty is largely obviated. In fact, with very pure ores it is sometimes best to keep out all fluxes, till reduction is complete, and add them afterwards.

If the gangue of the ore be basic, *i.e.* carbonate of lime, or oxide of iron, from 5 to 10 grms. of silica is added, and if much silica be present oxide of iron is added, 2 to 5 grms. being employed. Fluor spar may be added if the slags are pasty.

Chrysocolla and other Silicates.—If these ores are treated like oxides, the loss is generally very great, especially with poor ores. It is best to convert them into a regulus by fusion with iron pyrites, and treat the regulus as in dealing with sulphuretted ores of copper. Take—

20	grms.	ore.
15	„	iron pyrites, free from copper.
20	„	sodium carbonate.
10	„	borax.
10	„	fluor spar.

Mix thoroughly, melt rapidly at a high temperature, and pour. As soon as the button has solidified, quench, and otherwise treat as directed for a regulus.

Arsenical and Antimonial Ores require careful treatment. They must be carefully stirred during calcination, to remove arsenic and antimony as completely as possible. In the case of antimony particularly, the roasting should be at a low temperature. The ore or regulus may also be fused with twice its weight of nitre, and extracted with water to remove the arseniate and antimoniate, and the residue assayed for copper. Or, if arsenic or antimony be left in at the end, the metal may be melted with salt till they are removed. When much antimony is present this entails much loss; 2 or 3 grms. of lead are sometimes added to combine with and remove it from the copper. The metal, after the addition of lead, which separates from the copper on pouring, may be liquated and the copper subsequently refined.

Stanniferous Minerals are dealt with like antimonial ores, viz. by extra washings. Tin seriously interferes with refining, the “eye” being difficult to produce. If tin be suspected, the regulus should be made very fine. By this means the tin is excluded.

Zinc gives trouble by causing the regulus to be difficultly fusible. Often the regulus collects badly, owing to the difficult fusibility of zinc sulphide. If the regulus collects, the zinc may be removed by remelting it with the slags, a little nitre (1 or 2 grms.) and 5 grms. of borax.

When zinc is suspected the roasting should be prolonged, to ensure the oxidation of the zinc, and decomposition of sulphate. Very strong heat should be employed in the fusion.

Iron, nickel, and cobalt readily pass into the slag.

Lead, by forming sulphate in the roasting, persists until the refining stage, where it is got rid of with some little difficulty.

WET ASSAY OF COPPER.

The processes for the determination of copper by wet methods are based on the following facts :—

1. **Cyanide Process.**—Solutions containing copper are rendered deep blue by the addition of ammonia in excess, and the colour is discharged by the addition of potassium cyanide, the quantity of cyanide required under satisfactory conditions being proportional to the amount of copper present. This also applies to the blue solution obtained by the addition of Rochelle salt, or other fixed organic matter, and excess sodium hydrate to a copper solution.

2. **Iodide Process.**—Cupric salts liberate iodine from potassium iodide. The liberated iodine may be estimated by means of a solution of potassium thiosulphate of known strength, sodium iodide and sodium tetrathionate being produced. Since the smallest trace of free iodine gives a blue colour with starch, its complete conversion into iodide can be rendered evident by adding starch to the solution. In practice starch solution is added while free iodine is present, and standard thiosulphate solution is run in till the blue colour disappears.

3. **Electrolytic Process.**—The copper is deposited from solution by electrolysis, and weighed as metal.

4. **Colorimetric Processes.**—The depth of the blue colour produced when ammonia is added in excess to a solution containing the metal is employed to determine small quantities of copper. The solution is made up to a definite volume and compared with solutions of similar volume containing a known weight of copper. Sometimes potassium ferrocyanide is employed instead of ammonia.

5. Occasionally copper is precipitated from solution by sodium hydrate, by sulphuretted hydrogen, or by potassium sulphocyanate, and weighed as the oxide, or as the subsulphide (Cu_2S).

Preparation of Solution.—The material having been sampled, must, if an ore, regulus, or any product other than metal, be reduced by grinding to a fine state of division, and must, at least, pass through an 80 sieve. The quantity to be weighed depends on the richness of the ore, and varies from 0.5 to 5 grms. Duplicate assays should always be made.

All oxidized materials may be dissolved in nitric acid, and when necessary carefully evaporated with hydrochloric or sulphuric acids to remove excess of nitric acid.

Sulphurized materials should be treated as follows :—Cover the finely powdered mineral with nitric acid, sp. gr. 1.2, and set in a warm place on the hot plate (it must not boil) for 10 to 15 mins. This

decomposes the sulphide, and the sulphur separates in a flocculent form. Then add hydrochloric acid, and heat carefully till the sulphur is yellow, taking care that it does not get hot enough to melt the sulphur, or the globule formed may enclose undecomposed sulphide. Cautiously evaporate when necessary, adding hydrochloric acid from time to time till the nitric acid is expelled. This method of procedure is preferable to the use of aqua regia ($3\text{HCl} + \text{HNO}_3$) direct.

Of substances containing over 30 per cent. Cu take 1 grm., 10 to 30 per cent. Cu take 2 grms., below 10 per cent. take 5 grms.

POTASSIUM CYANIDE ASSAY.

This method of assay is under corresponding conditions fairly accurate, and, on account of the simplicity of the operations, very largely employed. It is necessary that the following conditions be fulfilled :—

(a) The operations of standardizing and titration of the sample should be done at the same temperature, which should be about 15°C .

(b) The quantities of acid and ammonia used must be about the same in each case as the consumption of cyanide is affected by the quantity of ammonia and ammonium salts in the solution.

(c) The bulk of the solution should be approximately the same.

(d) Approximately the same time—about 20 mins.—must be taken for each titration.

(e) Silver, zinc, nickel, and cobalt must be absent from the solution. Silver is removed by adding hydrochloric acid drop by drop to the acid solution, and filtering off the precipitated chloride. Arsenic or antimony does not directly influence the result. Iron may be separated by precipitation with ammonia filtered and washed, the precipitate being dissolved in hydrochloric acid and reprecipitated. This must be repeated two or even three times if the amount of iron be large. The filtrates and washings are added together.

In cases where the amount of iron is very large, it is a common practice to leave the precipitated ferric hydrate in suspension in the solution. As the titration approaches the end, the ferric hydrate assumes its characteristic colour. It must then be allowed to settle, and the colour of the clear solution noted. When the iron is simply precipitated, and left in the solution during the titration, low results, varying from 0 in coarse copper to 2 per cent. in pyrites may be obtained, depending on the excess of ammonia, temperature of precipitation, and bulk. Some operators add ferric chloride to the copper standard solution before titrating, approximately to the same amount

as it exists in the sample to be assayed. This does not entirely overcome the difficulty, unless the amount of copper is also approximately the same. Some assayers prefer to filter the whole of the solution to remove the ferric hydrate, etc., when the colour becomes faint in running in the cyanide.

It is also easy to determine the end, by filtering a little of the solution into a test-tube when nearing the end, and looking down the tube at a white plate, a similar test-tube containing water being held alongside.

A better method, and one which must always be adopted in the presence of zinc, is to precipitate the copper with sulphuretted hydrogen, sodium thiosulphate, or zinc (see p. 70), and dissolve the precipitated sulphide, or metal, and titrate.

Preparation of Standard Solution.—Weigh out 35 grms. of potassium cyanide (preferably gold cyanide). Dissolve in water and dilute to a litre in a measuring-flask. The solution must be kept in a well-stoppered bottle.

Standardizing.—Weigh out two quantities of 0.5 grm. of pure electrolyte copper. Put each into a flask, and add 10 c.c. nitric acid, sp. gr. 1.2. Heat till dissolved, and boil off nitrous fumes. Add water, and neutralize with ammonia. There is no necessity to do this accurately, but add ammonia till it begins to produce a permanent precipitate. Then add 10 c.c. strong ammonia to each, and dilute to about 200 c.c.

Fill the burette (or burettes, if possible) to the mark with the cyanide solution, and run it drop by drop into the copper solution at the rate of about 5 or 6 c.c. per minute, with repeated shakings. Continue the addition of the cyanide until the solution becomes pale pink.* Observe this colour with care, for in order to carry out this process accurately it is necessary to conduct all determinations on the same lines. When the pink colour appears, let stand, and if it does not disappear in 5 minutes add a few drops more cyanide and again let stand. Many assayers always dilute to same bulk and finish at the pink tinge. In this case each must determine for himself the shade of pink which is to be taken as the end. The method of completely discharging the colour is more reliable.

Read burette, and calculate thus—

Reading of burette, 72.5 c.c. = 0.5 grm. Cu

$$1 \text{ c.c.} = \frac{0.5}{72.5} = 0.006897 \text{ grm. Cu}$$

* The last 2 or 3 c.c. must be run in with the greatest caution, to ensure good results. A titration should occupy from 15 to 25 mins.

or each c.c. of the solution used in subsequent experiments will indicate the presence of 0.006897 grm. of copper.

Assay of Blister Copper or Bottoms.—Weigh out two quantities of 0.5 grm. of the copper in drillings or chippings, and proceed exactly as in standardizing. The impurities present do not interfere with the accuracy of the method unless the metal is unusually impure. Titrate a standard copper alongside under similar conditions. If much silver be present it may be necessary to remove it.

Calculate results thus: 1 c.c. potassium cyanide solution = 0.006897 grm. Cu. Amount of cyanide consumed = 71.2 c.c.

$71.2 \times 0.006897 = 0.4910664$ grm. Cu in 0.5 grm. blister.

Then $0.5 : 100 :: 0.4910664$ per cent. Cu.

$$\frac{0.4910664 \times 100}{0.5} = 98.213 \text{ per cent. Cu.}$$

Or, if 0.5 grm. be taken, the amount of copper found multiplied by 200 gives the percentage.

For works' use a table of standards should be drawn up, showing the copper value of a cyanide solution, when used in titrating 0.5 grm. pure copper, giving differences for each 0.2 c.c., and a second column giving the percentage in 0.5 grm. for volume used.

Volume of Solution taken.	grms. pure copper. Standard 1 cc. =	0.5 grm. ore. Percentage.
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This should be framed, and hung in a prominent position over titration bench.

Another method of calculating is to simply state the volumes of cyanide used for the standard and assay respectively ; thus—

Volume of cyanide used for standard 72.5 c.c. = 0.5 Cu

“ “ “ “ assay 71.2 c.c.

$$\left\{ \begin{array}{l} \text{c.c.} \quad \text{c.c.} \quad \text{pure Cu} \\ 72.5 : 71.2 :: 0.5 \\ \text{wght. of sample.} \\ 0.5 \quad 100 \end{array} \right\} : \text{per cent. of copper.}$$

The use of a table, however, obviates calculations and possibility of mistakes.

Assay of Copper Regulus.—Redruthite, etc.—Finely powder and sift the regulus. Weigh out two quantities, 1 grm. each. Pour 20 c.c. nitric acid, sp. gr., 1.2, into each of two flasks. Carefully add the sample to the acid and stand in a warm place for about 10 to 15 minutes. Then add 10 c.c. hydrochloric acid in small quantities at a time, and heat till action ceases. Probably some sulphur will separate; but, if care be taken, it remains flocculent, and can be cleaned without difficulty. If overheated it will melt to a globule and possibly enclose some of the sulphide. In this condition its solution is very tedious, and it is better to remove the globule, put it in a small porcelain crucible, burn it, and treat the residue in the crucible with a few drops of nitric and hydrochloric acid, warm, and wash into the main bulk. When solution is complete or the sulphur clean, evaporate to expel nitrous fumes, dilute somewhat, neutralize with ammonia. Add 10 c.c. excess of ammonia, and titrate as before with constant shaking. If much iron be present the solution will have a dirty dark green colour at first, but as the addition of cyanide proceeds the foxy red colour of the precipitated ferric hydrate will become more and more pronounced, till at the end, it will assume its normal colour. Towards the end, the precipitate must be allowed to settle and the colour observed in the clear liquor. The presence of arsenic causes this precipitate to settle badly, owing to the formation of a finely divided basic ferric arsenate.

If any uncertainty arises as to the finishing point, filter off the precipitate when the titration is nearly finished, and complete the titration in the clear solution. Some operators always follow this plan. It is better as the extra time spent in filtration is often lost in waiting for the precipitate to settle. Do not filter at the commencement, unless the precipitate is dissolved and again precipitated and filtered.

Calculate results as before.

Assay of Copper Pyrites.—Erubescite and poor sulphides.—Finely powder and mix the sample. Weigh out 1 grm. erubescite, peacock ore, good pyrites, or poor regulus, and from 1 to 5 grms. of poorer materials.

Treat as above to obtain solution, using proportionately larger quantities of acid, or, with poor pyrites shake carefully into warm aqua regia and heat gently till dissolved. Evaporate off excess acid, dilute to about 100 c.c. and nearly neutralize with sodium hydrate, and heat to boiling. To the hot solution cautiously add sodium thiosulphate in crystals. A black precipitate of coppersulphide is thrown down, mixed with some free sulphur. Let settle, filter, and wash quickly. Wash down the precipitate into a flask or beaker, using as little water as possible.

Dissolve the precipitate in nitric acid or aqua regia, neutralize, add excess ammonia, and titrate as before.

NOTE.—The copper may be precipitated by sulphuretted hydrogen instead of sodium thiosulphate. In this case, the solution must be evaporated to dryness, with the addition of sulphuric acid to prevent volatilization of the chloride taken up with water, and a few drops of hydrochloric acid, saturated with sulphuretted hydrogen, and the precipitate rapidly filtered and washed with water containing sulphuretted hydrogen (to prevent oxidation), and treated as before.

Another excellent method of separating copper for estimation is by potassium sulphocyanate, given on p. 87.

Nickel, Cobalt, Manganese, Zinc, and other interfering metals are removed by this treatment. The former interferes seriously with the reaction.

Arsenical Ores.—In the presence of iron, arsenic does not interfere, being carried down as basic ferric arsenate on adding ammonia. The precipitate should be filtered (see p. 83). Arsenic and antimony may be removed from sulphide precipitates by warming with yellow ammonium sulphide or with caustic soda.

The removal of arsenic may also be effected by nearly neutralizing the original acid solution with soda, adding 10 c.c. of a 10 per cent. solution of sodium acetate and heating to boiling. The basic acetate of iron thrown down carries with it the arsenic as a basic arsenate. If iron is absent or in small quantity, a few drops of a ferric chloride solution must be added. For safety and rapidity it is better to dissolve this precipitate after one washing, in as little HCl (sp. gr. 1.1) as possible, and reprecipitate to separate any copper carried down. Wash this second precipitate, concentrate the washings if necessary, and estimate as before.

Bismuth may be removed by adding excess of ammonia. The precipitate thrown down should be filtered off, dissolved, and reprecipitated as before.

Assay of Copper Pyrites, with previous roasting to remove sulphur.

Weigh out 5 grms. of the finely powdered ore. Roast to oxide in a muffle on a scorifier, previously rubbed with rouge or hematite, stirring with an iron wire. Weigh the residue accurately. Grind in an agate mortar, and weigh out two quantities of from 0.5 gm. to 1 gm. Dissolve in dilute nitric acid, and proceed with the solution as in previous cases.

State results thus—

Weight before roasting, 5.0 grs.

„ after „ 3.75 „

Proportion of original sample taken for analysis, 0.5 gm. portions—

$$\frac{0.5}{3.75} \times \frac{5}{1} = \frac{5}{7.5} = 0.6666 \text{ gm.}$$

This calculation may be obviated by taking for the final estimation $\frac{1}{3}$ or $\frac{1}{10}$ of the roasted product, thus securing $\frac{1}{3}$ or $\frac{1}{10}$ of the original sample.

Estimation by Potassium Cyanide preceded by precipitation of the copper by zinc—Steinbeck's process.

Dissolve the ore in the usual manner, but dilute only to 90 or 100 c.c. Remove all excess of nitric acid by evaporation, or by adding a strong solution of ferrous sulphate acidulated with H_2SO_4 to the hot solution till no more red fumes are evolved. Boil for about 5 minutes. (Test a drop of the solution on a tile with potassium ferrocyanide for excess of ferrous salt.)

Filter off the insoluble matter, and to the filtrate add a rod of pure zinc resting on or attached to a piece of platinum foil. The precipitation is complete in from 25 to 45 minutes, the copper being thrown down, either adhering to the platinum or as a spongy mass. Remove the undissolved zinc from the solution. Wash the copper thoroughly by decantation, and dissolve it in 10 c.c. nitric acid; then proceed as in standardizing the potassium cyanide solution.

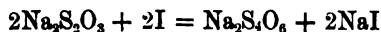
This process is applicable to complex ores, but is not very reliable, owing to the probability of fragments of undissolved zinc remaining with the copper.

IODIDE METHOD.

Estimation of Copper by means of a Standard Solution of Sodium Thiosulphate.—Cupric salts, when treated with iodide of potassium, liberate iodine. The precipitated cuprous iodide is insoluble in dilute acetic acid—



Thus 127 parts of copper in solution liberate 254 of iodine. Free iodine reacts with sodium thiosulphate, thus—



254 parts of iodine decompose 316 parts of thiosulphate, and the removal of the last trace of free iodine is rendered evident by the addition of starch solution—to which it communicates a deep blue colour—and running in the thiosulphate till the blue colour is discharged.

Preparation of Standard Solution.—Dissolve 30 grms. of sodium thiosulphate in water, and dilute to a litre.

Preparation of Starch Solution.—Take 0.5 gm. of finely powdered starch (white Glenfield, or arrowroot), and make into a smooth paste with 10 c.c. water. Heat 300 c.c. water to boiling, and gradually add the starch with constant stirring. Allow to settle and cool before use. The solution does not keep well, and should be prepared freshly each day.

Potassium Iodide.—This is best added in the solid state. Sufficient must be used to dissolve the iodine liberated. The minimum amount is about six times the weight of copper present, but in weak solutions more must be employed.

Standardizing.—Weigh out two quantities of 0.5 gm. pure copper. Dissolve in 5 c.c. nitric acid, and boil till all nitrous fumes are expelled. Neutralize with sodium carbonate, by adding a saturated solution of the salt till a slight permanent precipitate falls. Then add a little acetic acid (1 acid to 3 water) till the precipitate is dissolved, and cool. To the cold acetic acid solution add 3 grms. of potassium iodide, and shake till dissolved. The solution will assume a brown colour, and contain a white precipitate, which becomes apparent on settling. The brown colour of the solution is due to the iodine dissolved in the excess of potassium iodide employed. Titrate immediately with repeated shaking. As the thiosulphate is run in, the brown colour is gradually discharged. When it becomes pale, add 10 c.c. clear starch solution, and shake. A deep blue colour is immediately produced, and the titration may be proceeded with cautiously till the blue colour disappears. The end is wonderfully sharp, a single drop being sufficient to produce the final reaction.

This is probably the most accurate method in use for estimating copper. Few metals interfere with it. Iron in the ferric condition, as it exists in the solutions, must be present only in very small quantities, as ferric chloride also liberates iodine. Lead, mercury, and silver increase the consumption of iodide, but do not otherwise interfere. The former gives a yellow tinge to the precipitated cuprous iodide, due to lead iodide, which is somewhat objectionable owing to the tendency to run in too much thiosulphate before adding starch. Antimony and bismuth interfere, and if present in notable quantity must be removed.

The precautions to be observed are : (1) to keep the solution concentrated ; (2) to thoroughly expel nitrous fumes before neutralizing ; (3) to have only slight excess of acetic acid ; (4) to completely cool before adding iodide ; (5) to use starch free from floating particles ;

(6) the addition of sufficient iodide, and thorough agitation while titrating.

NOTE.—It often happens that the blue colour returns on standing for some hours. This may be disregarded, as it is due to secondary decomposition.

Determination of Copper in Alloys.—Blister copper, etc.

Weigh out two quantities, 0.5 grm. each, dissolve in 10 c.c. nitric acid, sp. gr. 1.2, and warm till no red fumes are evolved. Proceed exactly as for standardizing. In the presence of tin a white residue of metastannic acid remains on solution of the metal in nitric acid. It does not interfere except that it makes it more difficult to determine the point at which enough acetic acid has been added.

Determination of Copper in Ores, Mattes, etc.—It is better in these cases to separate the copper either by sulphuretted hydrogen, sodium thiosulphate, or zinc, as described (pp. 83, 84). Weigh out two quantities of from 0.5 to 5 grms. according to richness, dissolve, precipitate with sulphuretted hydrogen, filter, and wash as directed (p. 84). Dissolve the precipitate in about 20 c.c. of a mixture of equal parts strong nitric acid and water, taking care that nitrous fumes are completely expelled.

Dilute, neutralize with sodium carbonate, acidify with acetic acid, add iodide, and titrate.

GRAVIMETRIC METHODS.

Estimation of Copper as Sulphocyanate.—Cuprous sulphocyanate is insoluble in water and dilute hydrochloric acid, and as copper is the only metal precipitated by potassium sulphocyanate in hydrochloric acid solution, this is a convenient reagent for separating and estimating copper. Sulphurous acid gas or sodium bisulphite or metabisulphite is employed to reduce the copper to the cuprous condition.

Nitric acid destroys the reducing agent, and prevents the precipitation of the cuprous compound.

Preparation of Reagent.—Dissolve 50 grms. of potassium sulphocyanate and 50 grms. of sodium bisulphite or potassium metabisulphite ($K_2S_2O_5$) in water, and dilute to a litre. If tightly stoppered it may be preserved for months, but should not be exposed to the air.

Estimation of Copper in Bottoms and Blister Copper.—Dissolve 0.5 grm. in 5 c.c. nitric acid, add 20 c.c. hydrochloric acid, and evaporate to small bulk to completely remove nitric acid, or neutralize with soda and acidify with hydrochloric acid. Dilute to 25 c.c., filter off any silver that may be precipitated, and wash. To the warm solution

carefully add the sulphocyanate reagent till no further precipitate falls. Let settle, filter, and wash till free from hydrochloric acid. First wash with the precipitating reagent diluted, then with dilute ammonium acetate solution, and finally with water. Dry at 100° C. in water bath on a tared filter, and weigh. Factor for Cu = 0.5215. The precipitate may also be detached from the paper, transferred to a porcelain crucible, the paper burnt, and the ash added. It is then covered with pure sulphur and heated to redness in a muffle and weighed as Cu_2S . Factor = 0.7986.

Or the precipitate may be dissolved in nitric acid, evaporated nearly to dryness, taken up with nitric acid, and estimated by cyanide, iodide, or other process. In this case much of the washing may be dispensed with.

Assay of Ores or Mattes.—Dissolve as before (p. 79), but after evaporation, precipitate the copper as sulphide. Dissolve precipitate, and separate with sulphocyanate reagent, dry, and weigh, or dissolve and titrate.

Estimation of Copper as Cupric Oxide.—The copper in a solution, from which all other metals have been removed, may be estimated by adding caustic soda to the solution, boiling for some time, filtering, washing, and drying the precipitate. This is detached from the paper and set aside, the paper burnt, the ash received on the lid of a porcelain crucible, moistened with nitric acid, and evaporated to dryness. The precipitate in the crucible and lid are strongly heated, cooled in desiccator, and weighed. Factor for Cu = 0.7986.

Estimation of Copper as Subsulphide.—Precipitate the copper either with sulphuretted hydrogen or sodium thiosulphate in acid solution, as in previous methods. Filter and wash thoroughly. Dry the precipitate, detach it from the paper, and transfer to Rose's crucible or a porcelain crucible with perforated cover. Burn the paper and add the ash, cover with a layer of flowers of sulphur, and heat the whole to redness in a current of coal gas or hydrogen. If hydrogen be used, care must be taken to completely expel the air from the generating apparatus before placing the bunsen under the crucible. This method can only be employed in the absence of silver, mercury, bismuth, cadmium, arsenic, lead, antimony.

COLORIMETRIC METHODS.

In these processes the metal is estimated by comparing the depth of colour produced by a reagent with that produced by the same reagent in a solution containing a known weight of copper.

Estimation of Small Quantities of Copper by Potassium Ferrocyanide.—Very minute quantities of copper give a very decided chocolate-brown colour with potassium ferrocyanide. The delicacy of this test is only exceeded by the brown-black coloration given by sulphuretted hydrogen; but whereas the latter is interfered with by many metals which are likely to be present in slags, etc., *e.g.* lead, the ferrocyanide coloration is interfered with by few, and these may be easily removed. The reaction is rendered more sensitive by the presence of alkaline nitrates and chlorides.

Requisites.—(1) A standard copper solution; (2) a solution of potassium ferrocyanide; (3) burette; (4) two or more similar cylinders or white glass bottles (Nessler tubes answer well); (5) a 10 per cent. solution of ammonium nitrate.

Conditions of Working.—(a) The solution must be neutral and cold. If acid, a very slight excess of ammonia is added, and the excess removed by boiling, as the precipitate or colour is soluble in ammonia.

(b) Absence of iron. If present, this must be removed by precipitation with ammonia (see p. 80), and the precipitate dissolved and treated as there described.

Standard Copper Solution.—Dissolve 0.393 grm. of pure recrystallized copper sulphate in a litre of water, 1 c.c. = 0.1 mgrm. Cu.

$$\begin{array}{r} \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \\ 63.5 + 32 + 64 + 90 = 249.5 \\ \text{Cu} \\ \hline \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \end{array} = \frac{63.5}{249.5} = \frac{1}{3.93} \text{ or } 3.93 \text{ grms. of}$$

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ contain 1 grm. copper, and 0.393 grm. = 0.1 grm. copper in 1 litre = 1000 c.c.

$$\therefore \frac{0.1}{1000} = 0.0001 \text{ grm. or } 0.1 \text{ mgrm.}$$

Ammonium Nitrate Solution.—Dissolve 100 grms. of the salt in water, and dilute to a litre.

Potassium Ferrocyanide Solution.—Dissolve 3.62 grms. in 100 c.c. water.

Procedure.—From 5 to 20 drops of the ferrocyanide solution

(according to the copper present) is put into one of the comparison cylinders, and 5 c.c. of the ammonium nitrate solution added. The whole or an aliquot part of the neutral assay solution is added, shaken, and made up to 150 c.c. The same amount of ferrocyanide is put at the bottom of the other cylinder, 5 c.c. of ammonium nitrate solution added, and made up to 150 c.c. with pure water. The two cylinders are placed side by side on a white tile, and the standard copper solution added to the blank cylinder from a burette with constant shaking. When the depth of colour in the two cylinders is the same, the burette is read. Each c.c. = 0.1 mgrm. or 0.0001 gm. Cu. The copper present is calculated thus—

Volume of standard copper solution used	...	6.5 c.c.
Volume of solution (assay)	500 "
Amount taken	100 "
Weight of slag taken	5 grms.

$$6.5 \text{ c.c.} = 0.0065 \text{ gm.} = \text{copper in } \frac{100 \text{ c.c.}}{500 \text{ c.c.}} \times 5 \text{ grms.} = 1 \text{ gm.}$$

$$\frac{0.0065}{1} \times 100 = 0.65 \% \text{ Cu}$$

Estimation of Copper in Slags.—Finely powder the slag, weigh out 5 grms. and dissolve in aqua regia. Evaporate to dryness, take up with hydrochloric acid, add excess of ammonia, filter off the iron precipitate, dissolve it in hydrochloric acid, and reprecipitate with ammonia. Filter, and mix filtrates. Boil off excess of ammonia. Dilute to 500 c.c., take such a quantity that it contains not more than 1—1.5 mgrms. [slags from 1 to 1.5 per cent. take 100 c.c. *i.e.* $\frac{1}{5}$; slags 3 per cent., 50 c.c.; 3—6 per cent., take 25 c.c.], transfer to a cylinder with 10 drops of the ferrocyanide solution, add 5 c.c. ammonia nitrate, and make up to 150 c.c., and proceed exactly as in standardizing.

In dealing with slags that are not completely decomposed by hot aqua regia, weigh 2 grms. of the finely powdered slag, and mix it with 8 grms. of a mixture of sodium and potassium carbonates. Fuse in a porcelain crucible, and, after cooling, grind up the melted mass and the crucible. Transfer to a large porcelain dish, cover with dilute hydrochloric acid, evaporate cautiously to dryness. Take up with hydrochloric acid, and proceed with the precipitation with ammonia as before. This is the only safe and accurate method.

In comparing, look through the tubes at a white surface, but not

vertically, as the depths may vary somewhat. The tops of the tubes may be shaded by a piece of white paper held in front. Or, the colour may be judged by a light shining from behind, a piece of wet filter paper being placed there to equalize the light.

Colorimetric Estimation with Ammonia.—This method is largely adopted on account of its simplicity, for estimating small quantities of copper in slags, etc. It is somewhat less accurate than the foregoing method.

The copper solution is treated with excess of ammonia, and the depth of colour produced compared with prepared standards.

Preparation of Standard Tubes.—These may be large boiling-tubes, with a capacity of a little over 200 c.c., carefully selected, so as to be of uniform bore. Each must be provided with a tightly fitting cork well soaked in paraffin. Stoppered tube bottles may be used.

Dissolve 1 grm. of pure electrottype copper in 10 c.c. nitric acid, boil off nitrous fumes, make up carefully to 500 c.c. at 60° Fahr., each c.c. = 0.002 metallic copper. Fill a burette with the copper solution, and run 1 c.c. into a 200 c.c. flask, add 5 c.c. strong ammonia, make up to 200 c.c., and transfer to one of the comparison tubes, and cork tightly. It contains 0.002 grm. copper.

Make other tubes containing 0.004, 0.006, 0.008, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.024, 0.026, 0.028, 0.03 grm. of copper, containing respectively 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 c.c. of the copper solution. The tubes should be kept in a dark place.

Testing Ore Furnace Slags for Copper.—Treat 5 grms. of the finely powdered slag with 20 c.c. aqua regia, and boil till completely decomposed. Or fuse and dissolve as described above. Add a little water, neutralize with ammonia, and add 5 c.c. in excess. Dilute to 200 c.c. Transfer to a comparison tube, and let the precipitate settle. Compare the depth of colour with that of standard tubes by looking through with a moist filter paper behind. If the colour is the same as, say, that containing 0.018 grm. copper, 5 grms. of slag contain 0.018 copper. As 5 : 100 :: 0.018 : per cent. of copper in slag = $\frac{100 \times 0.018}{5} = 0.36$ per cent.

Another method of applying this principle, where rapidity is less important, is to take 12½ grms. (or other quantity) and dilute the solution, after adding ammonia, to 500 c.c. After thorough shaking, 200 c.c. of the liquid is filtered into a comparison tube. Care must

be taken to observe how much slag is represented by the 200 c.c. of solution taken thus with 12.5 grms.

$$12.5 \times \frac{200 \text{ c.c.}}{500 \text{ c.c.}} = 5 \text{ grms. taken}$$

Or the test may be conducted in the same way as the ferrocyanide test (p. 89). The solution should not contain less than 2 mgs. per 200 c.c., or more than 60 mgs.

Nickel interferes, as it also gives a blue solution with ammonia.

If time allows, the copper may be thrown down with sulphuretted hydrogen, the precipitate roasted to oxide and dissolved in 5 c.c. nitric acid, and the comparison made as before. Substances containing nickel may be treated in this manner.

Determination of Copper in Tin.—Weigh out 5 grms. of the tin. Dissolve in a beaker in 5 c.c. nitric and 25 c.c. hydrochloric acids. Evaporate to small bulk. Take up with dilute hydrochloric acid. Warm, and saturate with sulphuretted hydrogen. Filter off the precipitate and wash with sulphuretted hydrogen water. Warm gently with caustic potash or ammonium sulphide, filter and wash. Tin sulphide is soluble in ammonium sulphide. Dissolve the residual copper sulphide in dilute nitric acid, and estimate as before.

ELECTROLYTIC ASSAY OF COPPER.

Luckow's Process.—In this process the copper is precipitated from its solution by means of an electric current, the treatment being so managed that the metal is obtained as an adherent film on a platinum electrode.

Of the common metals, only silver, mercury, and bismuth interfere if the solution be acid. Mercury is precipitated before the copper, but amalgamates with it subsequently. Silver is almost simultaneously thrown down, while bismuth begins to be precipitated towards the end. These metals must be separated prior to electrolysis. Arsenic and antimony are not precipitated till some time after the complete precipitation of the copper.

Iron, zinc, nickel, cobalt, chromium, aluminium, calcium, barium, strontium, and the alkaline metals are not deposited in acid solution by weak currents. Lead and manganese are partially separated as peroxides at the positive electrode. Traces of manganese produce a violet colour in the solution from the formation of permanganic acid. This does not occur in the presence of organic matter or reducing agents.

In consequence of the simplicity of the manipulation, and the

accurate results obtained, this method of assaying copper ores has been very largely adopted.

Special Appliances required.—1. Battery. Some form of Daniell's cell is best. The gravity cell answers well, or the ordinary cylindrical form may be used. Lead-zinc elements are used at some works. Two pint cells will be required for one assay, and an additional cell for each additional assay. It is advisable to place the battery permanently in some convenient spot, and lead the connecting wires to a couple of binding-screws, or a switch, on the table where the assays are conducted. 2. Platinum electrodes for immersion in the copper solution, and which are connected with the battery. A piece of platinum wire, 0.04 in. thick and 12 ins. long, coiled to form a flat spiral with 4 or 5 ins. projecting up from the centre (Fig. 61), and a piece of stout platinum foil $2\frac{3}{4}$ ins. long and $1\frac{1}{4}$ in. wide, coiled into a cylinder (Fig. 62) $\frac{7}{8}$ in. diameter and $1\frac{1}{4}$ in. deep. This is riveted or welded to a stout wire, also of platinum. The wire electrode weighs about 5 grms., and the foil from 15 to 18 grms. A platinum dish or capsule may be substituted for the foil, in which case the wire is coiled into a wider spiral and the liquid placed in the dish for electrolysis. The dish is supported on a metal plate connected with the - (zinc) pole of the battery, and the spiral, supported from a clamp, with the + pole. Where many assays are done some special form of support is desirable. If foils and glass beakers are used, the stand shown in Fig. 63 is most convenient.



FIG. 61.

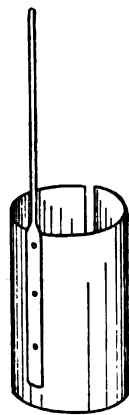


FIG. 62.

The bar, B, $\frac{1}{2}$ in. thick and 1 in. wide, slides up and down on the standards, and can be fixed at any desired height by the screws, S. Along its upper edge is fixed a brass strip with tongues bending over to the front side. This strip is connected with the + pole of the battery, and each of the tongues has a binding-screw attached. Under the lower edge is a copper strip, with similar tongues projecting into the spaces between the brass tongues, and also provided with binding-screws. The beakers stand in the holes below. The foils are attached to the copper—copper to copper—and the spirals to the brass. This arrangement allows the electrodes to be raised without arresting the current, thus preventing solution of the precipitated copper by the acid while removing the electrodes.

Mode of conducting the Assay.—Weigh out from 0.25 to 3 grms. of ore or regulus, the amount being so apportioned as not to contain more than 150 to 175 mgrms. of copper for an electrode or capsule of the size given. Thus, of a 60 per cent. matte take 0.25 gm., of a 10 per cent. ore, 1.5 grms.; of a 5 per cent ore, 3 grms. A generally safe quantity for pyrites is 2 grms.; coarse metal, 0.5 gm.; fine metal, 0.25 gm.; iron pyrites, 5 grms.

The ore must be finely powdered. Dissolve as before, with or without roasting. If bituminous matter is present, roasting is essential. The presence of chlorides in this assay is objectionable, and therefore care must be taken to remove hydrochloric acid by evaporating with sulphuric acid, when aqua regia is used as a solvent. Roasted ores may be dissolved in nitric acid and evaporated with sulphuric acid, 10 c.c. water

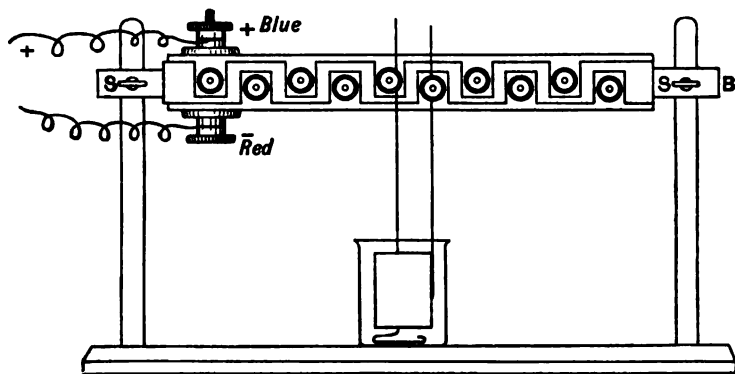


FIG. 63.

being added to dissolve the residue. A drop or two of nitric acid may be added to assist this. If silver, arsenic, mercury, and bismuth are absent, transfer the solution, without filtering, to the precipitating beaker. The beakers are about 2 inches high, flat bottomed, and have a capacity of about 75 c.c. Wash out carefully with small quantities of water and add the washings. The volume must not exceed 50 c.c. Add to each a few drops of a strong solution of tartaric acid. Weigh the foils, and clamp the wire spiral electrodes on the + terminals and the weighed and numbered foils, to the - terminals, so that the edge of the foil is $\frac{1}{10}$ inch above the spiral and clear all round. Place the beaker or beakers underneath, and lower the electrodes into the assays. The foils must not be more than three-fourths immersed. Switch on the current (or couple up the battery) and leave the assays for 8 hours. The temperature

must not fall below 60 to 70° Fahr. Oxygen gas will be liberated at the + and copper deposited at the - electrode.

Weighing the Assay.—When deposition is complete the solution will be colourless. Completeness of precipitation may be tested by adding a little weak nitric acid (1 in 10), and observing whether any copper deposits on the clean foil now freshly immersed. Remove each electrode separately, rapidly plunge it into a beaker of fresh water, and rinse well. (This plunge bath is to prevent the adhering acid solution from dissolving any copper owing to delay from any cause). Then wash the deposit with alcohol, either by immersion or with a wash-bottle, dry at 100°, and weigh.

The increase in weight = copper deposited.

The solutions in the beakers are tested for any remaining copper, and traces estimated by the colorimetric methods on p. 89, which see.

Removal of Silver.—This metal is separated as chloride, by filtering off the residue insoluble in aqua regia, after dilution, or by adding hydrochloric acid if it has not been used in the solution, prior to evaporating with sulphuric acid. The silver present may be estimated by scorification assay of the residue, if desired.

Removal of Arsenic.—This may be removed as basic arsenate of iron by methods given on p. 84, or, after deposition, the copper deposited may be dissolved in nitric acid and estimated by potassium cyanide or sodium thiosulphate.

Removal of Bismuth.—Add excess of ammonia, and filter off precipitate of bismuth hydrate, ferric hydrate, etc. Acidify the filtrate with nitric acid before electrolyzing.

SILVER.

THE estimation of the metal is usually required in the following substances—

- (a) Silver ores, and argentiferous ores of other metals.
 - (b) Argentiferous mattes and speiss.
 - (c) Argentiferous lead, copper, and copper alloys.
 - (d) Silver alloys.
 - (e) Gold alloys.
 - (f) Solutions.
 - (g) Burnt iron pyrites.
 - (h) Furnace slags, flue dust, cupel bottoms, litharge, residues from solutions. Electrolytic mud, silver mud from Claudet process. Muds from Van Patera, Russell, and other processes.
- (a) **Silver Ores.**—**Native Silver** occurs in grains, in strings like wire, (wire silver), and in platy or arborescent masses. It is white (tarnishes black), metallic, malleable, and easily cut with a knife. Crystallizes in the cubic system, although the crystals are always small. It constitutes the “metallics” of silver ores. Gold and copper are often present, and occasionally platinum, antimony, bismuth, and mercury. It is soluble in nitric acid, and fuses before the blowpipe. The particles are often so fine as to be quite invisible to the naked eye. Sp. gr., 10·5 ; hardness, 2·5—3.

Argentite, Silver Glance, Sulphide of Silver (Ag_2S), is a soft, sectile blackish-lead-grey, brittle mineral, with a metallic lustre. Its crystals are cubic, but it is commonly massive. The streak is lead grey and shining. There is some liability to confound this ore with redruthite and other copper ores and with lead ores. Before the blowpipe, it yields silver when heated alone (distinction from lead), is much heavier than copper ores, and is sectile. It contains, when pure, 87 per cent. Ag. Sp. gr., 7·3 ; hardness, 2·25. Usually, lead, copper, and iron are also present.

Stephanite, brittle silver ore, is an iron-black, antimonial sulphide of silver ($5\text{Ag}_2\text{SSb}_2\text{S}_4$) which yields silver before the blowpipe when mixed with carbonate of soda and incrusts the charcoal with a white film of oxide of antimony. Heated alone

it fuses to a dark globule. It usually contains about 70 per cent. Ag, and about 14 per cent. Sb, with Cu, etc. Sp. gr., 6·27; hardness, 2·25.

Polybasite is another antimonial silver glance, but containing arsenic, copper, and sometimes other metals ($8Ag_2SCu_4SA_2S_2$). Colour, iron black, streak black. It contains up to 75 per cent. of silver. Sp. gr., 6·2.

Frieslebenite is an antimonial ore containing lead, with a steely or leaden grey colour. It contains about 23 per cent. of silver. Sp. gr., 6·64.

Red Silver Ores.—**Pyrrargyrite**, dark red silver ore ($3Ag_2S, Sb_2S_3$), is a dark-red or blackish mineral, giving a cochineal red streak. It crystallizes in hexagonal forms, is brittle and soft, fuses before the blowpipe, and covers the support with oxide of antimony; yields silver when heated with carbonate of soda, or alone on prolonged heating. It contains 59·8 per cent. of silver. Sp. gr., 5·7–5·9; hardness, 2·5.

Proustite.—Light red silver ore ($3Ag_2S, As_2S_3$) is the corresponding arsenical compound. It is lighter in colour and streak. It gives an arsenical odour (garlic) before the blowpipe, and otherwise behaves like pyrrargyrite. It contains about 65 per cent. of silver. Sp. gr., 5·4–5·6; hardness, 2–2·5.

Miargyrite is a black antimonial silver sulphide, giving a red streak, containing only 36 per cent. of silver.

Naumannite, a selenide of silver (Ag_2Se), contains 73·2 per cent. of the metal; **encairite** (Cu_2SeAg_2Se), **Hessite** (Ag_2Te), **Petzite** ($AgAu$), **Te**, **Sylvanite** ($AuAg$)**Te**, **Sternbergite** ($AgFe_2S_2$), **Stromeyerite** (Ag_2S, Cu_2S), **Zanthoconite** ($3Ag_2S, As_2S_3$), are less commonly occurring silver ores.

Horn Silver.—**Kerargyrite.**—**Silver Chloride** ($AgCl$) is a soft waxy mineral of a greyish colour (sometimes greenish or bluish), which darkens on exposure to light, becoming nearly black. It has a resinous or adamantine lustre, a shining streak, and no cleavage. Cuts like wax or horn. The crystals are cubic. It fuses readily (in candle-flame), and yields silver when heated with carbonate of soda. Rubbed on a clean iron surface, it deposits silver. Sp. gr., 5·5; hardness, 1–1·5; and contains, when pure, 75·25 per cent. Ag.

The bromide and iodide of silver also occur.

The great value of silver allows materials yielding only small quantities of the metal to be treated for its extraction, hence it frequently happens that the characteristic properties of the pure mineral cannot be made out in the ore mass, except at isolated points and in very carefully selected specimens, while in many cases the ore is simply a lead, copper, or zinc ore containing silver.

(b) **Argentiferous mattes and speiss**, such as are obtained in copper and lead smelting, containing copper and sulphur, with or without iron, lead, arsenic, antimony, cobalt, nickel, tin.

(c) Lead from smelting furnaces, Pattinson pots, Parkes' retorts, etc., of varying richness.

Copper from smelting furnaces. Blister and bottoms copper.

Alloys, such as argentiferous German silver, etc.

(d, e) All alloys, consisting largely of silver, and of silver and gold.

(f) **Solutions.**—(1) Claudet solutions, containing copper, silver, iron, and lead chlorides. (2) Cyanide solutions: Electro-plating and depositing baths. (3) Thiosulphate solutions: Van Patera and Russell Lixiviation liquors, "Sweet liquor," containing silver, copper, lead, zinc, etc. (4) Silver sulphate and silver nitrate solutions obtained in the parting process.

(g) The pyrites cinders from the manufacture of vitriol, containing only traces of silver.

(h) Slags from furnaces, smelting silver muds and rich ores, consisting mainly of silicate of iron, with some lead, copper, etc., containing from 0.5 to 4 ozs. of silver per ton.

Silver mud from Claudet's process, consisting of metallic silver, copper, lead, zinc, and iron oxides, lime, and smaller quantities of other bodies, and containing from 6 to about 12.5 per cent. of silver.

Mud from the solution of copper in making copper sulphate, containing from 800 ozs. to 1500 ozs. of silver per ton.

Electrolytic mud from the electro refining of copper, containing up to 25 per cent. (8000 ozs. per ton) of silver.

Silver sulphide precipitate from thiosulphate lixiviation processes sometimes containing 85 to 87 per cent. of silver,

Russell mud, consisting of sulphides of silver, copper, and lead, and frequently containing not more than 4 to 6 per cent. of silver.

Flue dust, consisting of lead sulphate, sulphide, and oxide, zinc, arsenic, antimony, and other oxides, lime, etc., containing varying amounts of silver.

REACTIONS FOR SILVER AND ITS COMPOUNDS.

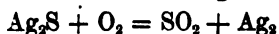
Dry Reactions.—The metal fuses before the blowpipe without oxidation to a brilliant metallic bead. As it cools, it frequently "spits," owing to the expulsion of dissolved oxygen.

The chloride, bromide, and iodide melt without decomposition, but are reduced when heated with sodium carbonate, yielding metallic silver without incrustation; thus—



The nitrate, sulphate, etc., are reduced by heating alone.

The sulphide is reduced in the oxidizing flame ; thus—



yielding metallic silver.

Wet Reactions.—Silver dissolves readily in nitric acid and in hot, strong sulphuric acid, but is insoluble in hydrochloric acid. It is blackened by sulphuretted hydrogen, and by alkaline sulphides, Ag_2S , being produced. The salts of silver, except the chloride, bromide, and iodide (and some organic compounds), are soluble in water or weak nitric acid.

In solutions of silver salts.

1. Hydrochloric acid gives a white precipitate of silver chloride (AgCl), which becomes curdy on boiling. The precipitate is insoluble in acids, but readily soluble in ammonia, potassium cyanide, sodium thiosulphate, and, less readily, in solutions of certain other chlorides.

2. Sulphuretted hydrogen precipitates black Ag_2S in solutions acidified with nitric acid. The precipitate dissolves in hot dilute nitric acid with separation of sulphur, but is insoluble in caustic soda or ammonium sulphide.

3. Caustic soda precipitates Ag_2O as a dark-brown precipitate, insoluble in excess.

4. Sodium carbonate precipitates silver carbonate Ag_2CO_3 , insoluble in excess ; soluble in nitric acid.

5. Potassium chromate produces a red precipitate of silver chromate (Ag_2CrO_4), soluble in nitric acid, and in caustic soda.

6. Potassium bromide throws down white AgBr , soluble, but with greater difficulty, in the same solvents as the chloride.

7. Potassium iodide precipitates yellowish AgI , sparingly soluble in ammonia.

8. Metallic silver is precipitated as a bright film, or as a grey or black powder by copper or zinc, from acidified solutions. Similarly, the insoluble chloride, bromide, and iodide are reduced by being moistened with hydrochloric acid and placed in contact with zinc.

DRY ASSAY OF SILVER.

The dry assay of silver is based on the following facts :—

1. All silver compounds are decomposed by fusion with sodium carbonate and metallic lead, or substances which yield metallic lead on fusion. The silver alloys readily with lead, so that the resulting lead button contains the silver. Other metals may also be reduced, and alloy with the lead.

2. The lead in the alloy may be removed by oxidation on a bone ash cupel, which absorbs molten oxide of lead, the silver being left.

The separation of other base metals which may be present is effected by taking advantage of the solubility of their oxides in fused litharge and consequent absorption by the bone ash. With a suitable proportion of lead complete separation may be effected. A sufficient excess of lead must be present to so prolong the operation as to permit of the complete oxidation of the base metal, while yet enough lead remains to produce sufficient litharge to effect the removal of the oxide formed.

In assaying alloys, the addition of sufficient lead prior to cupellation is often all that is needed. With poor alloys it is often better to separate the silver as chloride by a wet process instead of cupelling the alloy direct.

3. The earthy matters associated with the silver may be converted into fusible compounds by using suitable fluxes.

Methods of Assay.—Three processes are followed for the assay of silver bearing substances.

1. **Pot or Crucible Assay.**—The ore, or other material to be assayed, is mixed with (1) litharge, red lead, or white lead; (2) suitable fluxes; (3) some reducing or oxidizing agent as occasion may require. The mixture is melted in a crucible, and yields a button of lead which contains all the silver and gold, and small quantities of foreign metals. This button is scorified if necessary, and subsequently cupelled.

Sulphurous ores are usually roasted to remove the sulphur before fusion. The slags obtained are generally cleaned from silver by remelting (see p. 104). If the button of lead is too large, it is scorified to reduce its weight.

This method of assay is suitable for poor materials, as it permits of comparatively large quantities of the substance being treated.

2. **Scorification Assay.**—The substance is mixed with granulated lead, the quantity employed depending on the nature of the substance treated, and heated on an open dish in the muffle at a fairly high temperature. If a compound, it is decomposed either by the lead or by oxidation, and the silver is absorbed by the remaining lead. The operation is continued till a large proportion of the lead has been oxidized. This permits metals other than lead—tin, antimony, nickel—to be largely oxidized and removed by solution in the litharge prior to cupellation, with which operation they interfere. A button is thus obtained, which is easily cupelled. The litharge formed also serves as a flux for the earthy matters present. The contact of the molten litharge with the dish for so long a period produces serious corrosion, and to lessen it, and assist in promoting fluidity of the slags, a little borax is often added; this must, however, be used with care. Some assayers add a minute quantity of sodium carbonate in scorifying materials containing chloride or iodide of silver.

The lead button obtained is cupelled, and the slags cleaned if necessary.

Scorification is often resorted to for the treatment of buttons obtained in crucible assay to remove tin, antimony, etc., before cupelling. For this purpose, unless the button is too heavy, more pure lead must be added.

The method is suitable for rich materials and for copper ores and mattes.

3. **Cupellation** without previous reduction is employed in the assay of alloys of suitable character, and for the treatment of the buttons of lead obtained in crucible and scorification assays.

CRUCIBLE ASSAY.

The litharge, red lead, or white lead used must first be assayed for silver. 1000 grs. or 50 grms. of the lead compound is run down with argol, carbonate of soda, and borax (see p. 61), and the button cupelled. The amount of silver per 100 grs. or 10 grms. of the litharge, etc., should be noted down in a note-book, and on the jar containing the stock, so that the weight of silver contained in the quantity used may be deducted from the silver obtained in the assays.

As the reducing power of various reducing agents is somewhat uncertain, this must be determined by experiment. The following mixtures should be made and melted, taking care that no coke falls into the crucible.

EXPERIMENTS TO DETERMINE REDUCING POWER.

	1	2	3	4
Litharge	400	400	400	200 parts
Argol	10	—	—	—
Flour	—	10	—	10
Charcoal	—	—	10	—
Carbonate of Soda ...	200	200	200	100
Borax	25	25	25	—
Nitre	—	—	—	5

In 1, 2, and 3, divide the weight of lead obtained by the quantity of reducing agent employed, and compare their relative reducing powers. In 4, obtain the difference between 2 and 4, and divide by the weight of nitre employed. This represents the relative oxidizing power of the nitre. At least two sets of experiments should be made.

In dealing with sulphurous ores, the sulphur is best removed by roasting prior to fusion, as the sulphides react on the litharge, etc., and reduce lead,* so that the button would be too heavy, little or no lead would be left in the slags, and the button would probably contain sulphur, or even a regulus containing silver might be formed.

* Thus 1 part of iron pyrites reduces	8.5 parts of lead
„ 1 „ copper pyrites, mispickel, blende, and grey copper
ore reduce	7
„ 1 „ antimonite reduces	6
„ 1 „ galena	3

In some cases, instead of roasting, nitre is added in the charge. It is then necessary to first determine the reducing power of the ore by running down 50 grs. or 2·5 grms., with litharge and fluxes, and weighing the lead button obtained.

One part of nitre oxidizes or prevents the reduction of 4 parts of lead. Hence, if 2·5 grms. of the material treated with 30 grms. of litharge and 2·5 of sodium carbonate produce 15 grms. of lead, 25 grms. would produce 150 grms. of lead if sufficient litharge were present. Since only about 20 grms. of lead is required, the reduction of 130 grms. must be prevented by oxidation of the reducing agent. This can be effected by adding $\frac{130}{4} = 32\frac{1}{2}$ grms. of nitre to the charge.

The preliminary examination must be conducted on the same lines as the actual assay.

In case the quantity of lead reduced is insufficient, charcoal or flour must be added to produce the necessary amount on the basis of the experiments previously made, or roughly—

			Weight of lead from litharge.
1	gram. charcoal reduces	...	23 grms.
1	„ flour (dry)	...	12 „
1	„ tartar (argol)	...	4-6 „

If red lead be used, the quantity of reducing agent to be added will be greater, on account of the larger proportion of oxygen it contains ($\text{PbO} : \text{Pb}_2\text{O}_3$). Thus, the amount of reducing agent required, assuming that the substances are completely reduced, is as 3 : 4. *E.g.* 1 grm. of charcoal reduces 24 of lead from litharge, and is capable of reducing 18 grms. of lead from red lead if no excess of red lead be present, but if the red lead be in excess, then the quantity is reduced thus, $\text{Pb}_2\text{O}_3 + \text{Pb} = 4\text{PbO}$, *i.e.* 685 grms. of red lead convert 207 of lead into litharge, or for about every 3·5 grms. of red lead in excess in the mixture 1 grm. less of lead will be obtained. The composition of red lead is, however, more often $3\text{PbOPbO}_2 = \text{Pb}_3\text{O}_4$ than Pb_2O_3 , and consequently about 4·5 grms. in excess oxidizes 1 grm. lead, while in practice the ratio is put at about 5 : 1. In calculating the amount of charcoal or flour to be used, supposing the assay mixture to contain 50 grms. of red lead, 10 grms. ($\frac{50}{5}$) less lead will be obtained than if litharge were employed. Add this to the quantity of lead required, say 25 grms., thus $25 + 10 = 35$, and add sufficient charcoal to reduce that quantity (since 1 grm. reduces 23) $\frac{35}{23} = 1\frac{11}{23} = 1\frac{1}{2}$ approximately.

The action of red lead in counteracting the reducing power of sulphides causes less nitre to be needed when that body is substituted for litharge. Since the oxidizing power of nitre is 4 (1 part oxidizes 4 of lead), and that of red lead is $\frac{1}{5}$, therefore 1 part of nitre equals 20 parts

of red lead in oxidizing power, and 1 grm. less nitre must be added for each 20 grms. of red lead employed.

The presence of peroxides, as of manganese and iron, also diminishes the amount of lead reduced. Ferric oxide reduces it by a quantity equal to 1.25 times the weight of the oxide present.

In making up the charges, it is safe to calculate on a button weighing about 20 grms. Many assayers calculate on a button of lead varying with the weight of ore employed, but this is seldom necessary.

The charges employed vary greatly with the nature of the ore. With silicious ores containing little iron or other oxides, there is no advantage in leaving much lead in the slag. The only necessary condition is to have the slag fluid. With a large proportion of earthy and other oxides, as in roasted pyritic ores, it is necessary to add excess borax or sand and glass, unless a large excess of lead oxide is employed, by which means the earthy oxides are fluxed. In the presence of oxides of iron, copper, and other metals, an excess of litharge prevents reduction and secures a purer button than is obtainable in any other way.

The fluxes employed vary with the gangue. Carbonate of soda or litharge is best for quartz, 2 parts of soda, or 4 to 5 parts litharge, to 1 of quartz. Borax and sand are best for lime, oxide of iron, etc. With ores containing oxide of iron, etc., it is necessary to make a preliminary assay with reducing agent added.

The fusion should be conducted at a full red heat, *i.e.* at as low a temperature as will secure fluidity of the slags. The temperature should be gradually raised, especially when much litharge is used, otherwise the fluxes may melt before the assay, and running down, leave it as a hard infusible mass floating in the denser flux and give much trouble. The introduction of soda, in place of some of the litharge, is an advantage on this account, as it has less tendency to liquefy from the mass. Hence, while it is difficult to give charges suitable for all cases, general charges may be given, which must be modified as occasion requires, as shown by the behaviour during a preliminary experiment.

I. Charge for quartzose ores, free from pyrites, oxide of iron, etc.

Powdered ore	...	400	grs., or 20 grms.
Litharge	...	600	" 30 "
Sodium carbonate	...	600	" 30 "
Borax	...	100	" 5 "
*Charcoal	...	20	" 1 "

* Or its equivalent in flour.

Clean the slags by grinding and remelting, with 20 grms. of litharge and 1 gm. of charcoal in the same pot, which should be put back into the furnace after pouring, and the mixture charged in with the copper scoop. Carefully detach the slag by hammering on the edges. Hammer both buttons into cubes, with rounded corners, and edges and cupel.

II. Charge for ores containing metallic oxides and silicious matter.

Powdered ore	...	400 grs., or 20 grms.
Litharge	...	1000 " 50 "
Sodium carbonate	...	800 " 15 "
Borax	...	200-300 " 10-15 "
*Charcoal	...	35-40 " 1.75-2 "

Cover with a layer of salt, and heat as before. Clean the slags and cupel the buttons. Ores containing barytes or phosphate of lime yield a thick slag, which is difficult to pour. In this case about 5 grms. of powdered flour spar may be added to the charge.

III. Charges for ores containing sulphides. These will vary with the nature of the sulphide present.

For quartzose minerals containing but little iron pyrites, galena, blende, or mispickel, red lead may be substituted for litharge, and the amount of charcoal or flour reduced—

Powdered ore	...	400 grs., or 20 grms.
Red lead	...	600 " 30 "
Carbonate of soda	...	600 " 30 "
Borax	...	100 " 5 "
Charcoal	...	15 " 0.75 "
or flour	...	30 " 1.5-2 "

If much foreign sulphide is present the quantity of reducing agent may be further reduced or altogether omitted, as the sulphur will reduce sufficient lead. See p. 101.

IV. Charge for sulphides (unroasted), using iron as a desulphurizer.

Powdered ore	...	400 grs., or 20 grms.
Red lead	...	600 " 30 "
Carbonate of soda	...	600 " 30 "
Borax	...	100 " 5 "
Argol	...	60 " 3 "

and a strip of iron or 3 nails.

* Or its equivalent in flour.

Treat as for the assay of galena, and pour. Clean and cupel the button. A large button generally results.

NOTE.—The use of iron cannot be recommended, as the mattes formed may carry silver.

V. Charge for sulphides (unroasted), with nitre as a desulphurizer. Pure pyrites reduces $8\frac{1}{2}$ times, copper pyrites and blende 7 times, antimony sulphide, and grey copper ore, polybasite, etc., about 6 times, and galena nearly 3 times its weight of lead. Nitre, as will be found on reference to results of experiments, p. 101, prevents the reduction of about 4 times its weight of lead, therefore about $2\frac{1}{2}$ times its weight of nitre will be required to completely oxidize iron pyrites, $1\frac{1}{2}$ times for antimony, etc., $1\frac{3}{4}$ for copper pyrites, and about $\frac{2}{3}$ for galenas. It is better to use rather less nitre than is required, and leave sufficient sulphur unoxidized to reduce the necessary amount of lead, and sufficient oxide of lead to prevent any sulphur passing into the lead button.

Preliminary assay—

50	grs., or	5	grms. ore
500	„	50	„ red lead
50	„	5	„ soda

Cover with salt, to exclude furnace gases. Weigh the resulting button. Assuming that the weight of lead required for cupellation is equal to the weight of ore assayed, deduct 50 grs. or 5 grms. from the weight of lead obtained, and divide the remainder by 4, or by the equivalent previously obtained. The result gives the weight in grains or grams. of nitre to be added. If the amount of lead reduced falls short of the required weight, flour or charcoal must be added to produce it.

Examples.—Weight of lead obtained by preliminary assay = 35 grms. $35 - 5 = 30$ grms. in excess, $\frac{30}{4} = 7.5$ grms. of nitre are required for each five of ore, or $\frac{7.5}{5} = 1.5$ times the weight of ore, and the charge would be made up as follows :—

Weight of ore	400	grs., or	20	grms.
Red lead, according to quantity of lead reduced	1000–2000	„	50–100	„
Carbonate of soda	400	„	20	„
Nitre	600	„	30	„
Borax	100	„	5	„

Cover with salt.

Less nitre than this suffices for most silver ores, but the quantity must be determined.

VI. Charge for Roasted Sulphides—ores and mattes.

Weight of ore, or matte	100–400 grs., or 5–20 grms.
Sodium carbonate ...	100–400 „ 5–20 „
Litharge ...	500–2000 „ 25–100 „
Glass borax ...	200–800 „ 10–40 „
Charcoal ...	20–35 „ 1–2 „

The fusion and other operations are conducted as before. The larger proportion of litharge is employed to aid in carrying the copper oxide, etc., into the slag.

N.B.—Buttons for cupellation must be soft and malleable. Sulphur in the button is due to incomplete roasting or insufficient nitre, and frequently renders the button brittle. If the buttons are not malleable they must be scorified with the addition of about half their weight of granulated lead, and the operation repeated if necessary till a malleable button is obtained.

SCORIFICATION ASSAY.

In this method of assay the material is mixed with excess of granulated lead, sometimes with the addition of borax, and heated in an open dish in an oxidizing atmosphere. By this means the silver compounds are decomposed, either by the direct action of the lead or by oxidation, the liberated silver alloying with the lead, and the foreign oxidizable metals present are converted into oxides, which are dissolved and removed by the litharge formed by the oxidation of the lead. At the end of the operation there is left in the scorifier a lead button weighing much less than the lead used, but containing the whole of the silver in the ore, and a slag, consisting of litharge, and silicates, and borates of lead and other metallic oxides containing mere traces of silver. After cleaning the slags the buttons are cupelled. The method is especially applicable to the treatment of rich materials, but yields good results with all classes of ores.

The dishes employed, Fig. 28, are made specially thick, and of fine grain, to resist the corrosive action of the litharge, etc., and in various sizes.

Scorification of Ores, etc.—The sample and the necessary amount of test lead (see table, p. 108) are weighed out, together with the borax required (if any). The lead is divided into two portions, and the sample mixed with the borax and one half of the test lead and placed on a scorifier. The remainder of the lead is laid on the top. A

scorifying dish of such size that the charge barely fills it must be used. A dish $2\frac{1}{4}$ ins. in diameter suffices for a 50-grain (3.24 grms.) charge of ore. The variation in the weight of lead used is based on the quantity of oxide of lead required to flux off the associated gangue, or the metallic oxides resulting from the scorification, into the slag, so as to leave a button of lead, in which the silver, etc., is concentrated, and pure enough to cupel satisfactorily. Thus, it is possible to cupel argentiferous copper directly, with sufficient lead to carry the copper oxide formed into the cupel, but greater loss is likely to occur. It is therefore preferable to scorify with lead and remove most of the copper prior to cupellation. In scorification the lead by remaining in contact with the slags tends to diminish the loss that would arise from absorption by the cupel. See Cupellation.

If chloride or iodide of silver be present in the assay, some carbonate of soda is required to effect its reduction and prevent volatilization. See Silver Muds, p. 109.

The Operation.—The charged scorifiers are placed, by means of the scorifier tongs, in a muffle at a very bright red heat. The charge fuses, and generally the ore can be seen floating on the top. Any sulphur, arsenic, or other oxidizable matter is oxidized while the lead oxide formed dissolves any metallic oxides produced, and reduces them to a state of fusion, thereby liberating any silver which may be retained by them and causing it to pass into the lead. During this period the temperature should not rise too high, as the object is to pass as much of the oxidizable metals as possible into the slag, and as little as possible into the lead. The slag produced by the litharge, borax, etc., first forms a ring round the molten lead, the eye of which should appear quite clearly. As the operation proceeds, the ring of slag gradually extends over the surface of the button, and ultimately closes over it. During the final stages the temperature may be increased considerably, and at the end an almost white heat should be employed to ensure complete liquefaction of the slag. It should be very fluid, but if refractory a little more borax glass should be added. The fluidity may be ascertained by dipping a heated bent iron rod into the slag, lifting it up over the dish, and observing how the liquid slag drops off. Some assayers clean the slags at the end of the scorification by dropping a few grains (3 to 5) of anthracite wrapped in paper into the assay at this point, and waiting till action ceases. The lead precipitated from the slag is relied on to carry down any silver it may contain. This answers fairly well for simple ores, but with materials containing much foreign metals where great accuracy is required the slag should be cleaned by fusion in a crucible (see p. 104).

When the scorification is completed, remove the scorifiers and pour into button moulds. Detach the slag, clean and hammer the button, and cupel.

Successful scorification depends on having the muffle hot enough in the latter stages and the slags very fluid.

Scorification is resorted to for dealing with the impure lead buttons obtained in the crucible assay, in order to remove tin, antimony, copper, sulphur, etc. From $\frac{1}{2}$ to $1\frac{1}{2}$ times the weight of lead should be added and scorified down to a suitable weight.

CHARGES FOR SCORIFICATION.

Nature of material.	Weight of sample.		Weight of test lead.		Weight of borax.	
	grs.	grms.	grs.	grms.	grs.	grms.
<i>Ores—</i>						
Silicious and clayey ...	50	5	600-750	60-70	5-10	0.5-1
Do. mineralized ...	50	5	600-800	60-80	0-7.5	0-0.75
Ferruginous and limey ores ...	50	5	400-500	40-50	15-25	1.5-2.5*
Cupreous and fahl ores...	50	5	750-1000	75-100	0-7.5	0-0.75
Antimonial ores ...	25	2.5	400	80	50	5
Galena silicious ...	50	5	300-500	30-50	7.5-15	0.75-1.5
Tailings from amalgamation ...	100	10	600-750	60-70	0-15	0-1.5
Lead speiss ...	50	5	500-1000	50-100	8.5-12.5	0.85-1.25
Arsenical ores ...	50	5	500-800	50-80	0-25	0-2.5
† Stanniferous ores ...	50	5	1000-1500	100-150	7.5-12.5	0.75-1.25
Nickel ores and speiss ...	50	5	900-1000	90-100	7.5-10	0.75-1
Cobalt ores ...	50	5	900-1000	90-100	7.5-10	0.75-1
Zinc blende and zinciferous galena ...	50	5	500-850	50-80	7.5-15	0.75-1.5
Sweepings and hearth bottoms ...	50	5	400-700	40-70	5-10	0.5-1
† Slag and flue dust ...	50	5	600-750	60-75	5-7.5	0.5-1
Brass ...	50	5	1000-1250	100-125	7.5-10	0.75-1
† Bronze ...	50	5	1000-1250	100-125	10-12.5	1-1.25
† Gun Metal ...	50	5	1000-1250	100-125	10-12.5	1-1.25
† German silver ...	50	5	1000-1250	100-125	12.5-20	1.25-2
† Tin ...	50	5	800-900	80-90	8-10	0.8-1
Copper ...	50	2.5	900-1000	45-50	0-5	0.1-0.25
Iron (treat with nitric acid, evap. dry) ...	50	5	400-600	40-60	2.5-5	0.25-5

* A further addition of borax must be made at the end if necessary.

† The scorification is repeated until the button is soft enough for cupelling.

‡ Many assays (up to twenty or more) are made, and the buttons scorified together and then cupelled.

Scorification Assay of Claudet Mud.—Two grammes of the substance are scorified with 20 grms. of granulated lead, 5 grms. of litharge, 0.25 grm. carbonate of soda, and a little borax. The substance is mixed with

5 grms. of the lead, the litharge, and sodium carbonate, and placed on the scorifier. The remainder of the lead and borax are put over it and the scorification conducted in the usual manner.

NOTES.—In dealing with slags, fine dust, and other poor materials, it is necessary to make a number of assays. The resulting buttons are then scorified together into one prior to cupellation, a little borax being added. The final button should weigh about 25 grms.

Argentiferous iron should be oxidized with nitric acid, or by roasting prior to scorification. The buttons should be perfectly soft and malleable. Antimony, tin, arsenic, copper, and nickel among common metals, which harden lead exert an injurious effect on the cupellation, and should be completely removed by further scorification.

CUPELLATION.

This process, by which silver is separated from its alloy with lead and other oxidizable metals, differs from scorification in being conducted in a porous cup or dish which absorbs the molten litharge as fast as it is formed, thus keeping the surface of the assay clear and exposed to oxidation. Some of the litharge passes off as fume. Foreign metals present are oxidized during the cupellation either by the air or by the litharge formed. The fused litharge dissolves these, and carries them into the cupel except in the cases of antimony, tin, nickel, and zinc. Antimony forms an infusible antimoniate in the early part of the operation, which remains as a scoriaceous orange red ring round the side of the cupel, which is also often cracked. Tin forms a yellowish grey sintered infusible mass, and nickel a brown infusible porous residue. The formation of infusible substances leads to low results, since the lead, instead of remaining in one button of gradually diminishing size as the oxidation proceeds, is separated into globules which remain scattered through the mass, and though the oxidation of these may be complete, the silver they contain is not collected into one button. In such cases the lead button should be scorified with addition of lead and borax prior to cupellation.

The Cupels.—Bone-ash cupels for assaying purposes are made by moistening the very finely ground, sifted bone-ash with sufficient water to make it cohere when strongly compressed. This must be done by sprinkling with water, rubbing it well through the hands, and breaking up all lumps. The damp powder is then sifted through a 20 sieve, in order to thoroughly mix it and remove wet or hard lumps. The body of the mould (Fig. 30) is charged with sufficient of the bone-ash, the die put in, and either struck smartly with a mallet, or forced in by a screw press to consolidate the bone-ash. The die receives a twisting motion before withdrawal, in order to smooth the surface of the cupel, and after its removal, the false bottom

of the mould is pushed up, and the cupel placed on a sheet-iron tray to be thoroughly dried. The mould should be kept bright. Sometimes the body of the cupel is made of coarser material than the surface. In that case the two qualities are damped separately, and in charging the mould it is topped up with the finer ash. Some practice will be necessary before good cupels which do not crack in use can be made. Attention should be paid to the amount of water used, and the pressure employed to consolidate them. Cupels can, of course, be bought. They should be thoroughly dried before use. A cupel will absorb the litharge from approximately its own weight of lead.

The Operation.—The muffle should be uniformly heated to a little above the melting point of silver. The necessary cupels are placed in rows. Anything adhering to the surface of the cupels should be gently rubbed off with the finger, before putting them in the muffle. An extra row or two of blank or old cupels should be put in front, and if the back of the muffle is too hot the same should be done there. The cupels should be allowed to become thoroughly heated, and the buttons dropped into them in order from an iron tray, with numbered divisions, corresponding to the positions of the cupels in the muffle (Fig. 64),

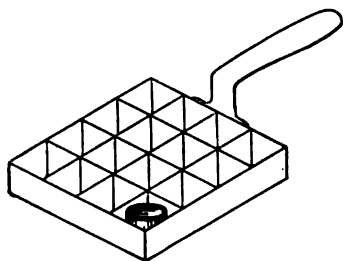


FIG. 64.

beginning with the front row, to ensure the completion of all the assays at one time. This must be done quickly to avoid cooling. Then close the muffle door, attend, if necessary, to the fire, and see that it is in such a condition as not to need replenishing during the operation. Watch the assays. A film of oxide first forms on the molten lead, and the cupel and contained lead can scarcely

be distinguished from each other. In a few moments a sort of gyratory motion commences, and gradually the film of litharge "throws off" and is absorbed by the cupel, the assay presenting a metallic, fuming, glowing surface, quite distinct in appearance from the cupel. The lead is, in fact, hotter, due to the oxidation going on. This is known as "uncovering" of the assay. Occasionally it does not occur, but an incrustation of litharge forms which prevents the operation proceeding, and the buttons are said to be "frozen." Generally this is the result of the temperature being too low. The difficulty may be got over by increasing the temperature, by holding a piece of glowing charcoal over the assay, or by putting a piece of wood or charcoal beside the cupel. The results obtained, however, in such cases are not reliable. An improvement is

effected by adding, as soon as the assay (after being frozen) has uncovered, a quantity of lead sufficient to cover the cupel higher than before.

When "uncovered" the cupellation should be allowed to proceed at a temperature a little below the melting point of silver. For this purpose the heat may be moderated and the door partially opened. (Some assayers cupel with a closed muffle. This has some advantages, but many disadvantages.) The difference between the molten lead and the cupel should be easily seen. If not, the muffle is too hot. The fumes from the cupels should not rise rapidly to the muffle crown (too hot) nor sink sluggishly to the bottom (too cool), but should hover round and above the cupels, and pass away slightly above their level. Much care is required in regulating the temperature so as to secure the best results. Gas muffles are most uniformly heated, but can only be trusted to work up to the melting point of silver, though occasionally higher temperatures are obtained. Coal muffles, with proper attention, work well. Coke muffles are liable to variations in temperature, and require careful firing. It must be borne in mind that the temperature of cupellation is much lower than that required for scorifying, and while both operations are very often conducted in the muffle at the same time, the scorifiers being placed at the back and hotter part, and the cupels in the front cooler portion, great judgment is required to adjust the relative positions of the scorifiers and cupels, to secure accurate results.

When cupellation is nearly complete, the temperature should be gradually raised to the melting point of silver or a little above it. As the last portions of lead "pass" from the silver, considerable apparent agitation of the button takes place, often with a display of rainbow colours. Finally the agitation ceases, and the button suddenly appears to settle itself and flash out brightly.

As soon as the assays have "passed," they are ready for removal, but trouble arises from the tendency of silver to "spit" or "vegetate" on solidifying, throwing off particles of the metal and occasioning loss. Buttons less than $\frac{1}{2}$ a millimeter in diameter are little likely to spit. To avoid loss, the assays should be cooled slowly by drawing them towards the open door for a minute or two prior to removal.

A good plan is to have ready a number of old cupels, previously heated, and to put one over each assay, removing the two together from the muffle. The cupels should be returned to the tray in the order they occupied in the muffle. The muffle is closed, the fire made up, and the next batch of cupels introduced ready for use.

If the temperature at which the operation has been conducted has been satisfactory, the button has a bright silvery lustre on the top, and

a dull silvery white lustre underneath. If the finishing temperature has been too low the surface is bluish and dull, and the button is coated with a yellow or greenish coat of litharge. If the temperature has been too high, the surface is mottled and sunken, the button is very liable to spit, may adhere strongly to the cupel, often has rootlets, and is sometimes spongy at or near the bottom. The silver button contains generally about 0.02 per cent. of lead.

Examination of prills and cupels.—The silver beads obtained vary in appearance according to size. Small buttons, not much more than a millimeter in diameter, should be nearly spherical in form, and adhere

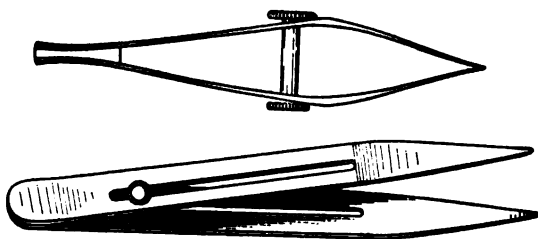


FIG. 65.

slightly to the cupel. Larger buttons will be flatter, but the edges should be well rounded. A flat button indicates the incomplete removal of impurities. This is specially so with copper, and in some cases the button may adhere strongly to the cupel. The surface should present a slightly crystalline appearance, and the button should adhere slightly, but be free from rootlets. Buttons which do not adhere

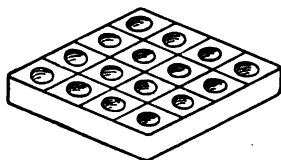


FIG. 66.

may contain lead. The prill should be detached by the forceps, a useful form of which is shown in Fig. 65, and any adhering bone ash removed by brushing and gently tapping. The cleaned beads should be placed in a wooden tray (Fig. 66) with cavities numbered to correspond with the cupel tray and weighed. If buttons from the cleaning of slags have been cupelled, the resulting prill should be added to the main bead and the two weighed together. If lead or litharge containing silver has been used in the assay, a deduction must be made from the weight of the button equal to the amount of silver thus introduced.

The cupels should be carefully examined with a lens (Fig. 67), to see that no small prills have separated from the main button.

If this has occurred it is hardly possible to collect them. The cupel must be melted as directed below. Good cupels show little or

no scouring action of the litharge (concentric rings or holes corroded from the sides), and if the temperature has been correct, little, if any, litharge will be left unabsorbed. The cupel may present a glistening appearance, due to small crystals of litharge, which must not be mis-

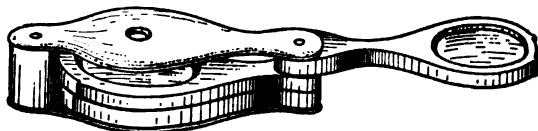


FIG. 67.

taken for prills of silver. Cracked cupels indicate bad making, insufficient drying, or the presence of antimony.

Cupels suspected of containing silver should be melted in crucibles as directed (p. 62), with an addition of 25 grms. of litharge, and the button cupelled.

Cupellation loss.—Loss arises from (1) cracking of the cupels and loss of lead and silver in the cracks; (2) corrosion of the surface of the cupel, by which portions of the lead become detached and cupel separately; (3) formation of unabsorbed crusts of litharge or scorixæ retaining lead, the silver from which remains entangled; (4) the mechanical removal of silver (possibly as oxide) by the litharge absorbed by the cupel; (5) the loss by volatilization in the fumes; (6) loss by “spitting” while cooling.

These sources of loss may be largely avoided by the use of good, well-made cupels and careful regulation of the temperature; cupels should not be too open in texture, nor yet too close (close cupels are liable to crack). They should be uniformly hard. The loss by volatilization is greater the higher the temperature employed and the longer the time occupied in cupellation. The loss by absorption is also somewhat greater under these circumstances, as the litharge, being more fluid, is more rapidly absorbed.

The actual loss in the cupellation of buttons from ore assays, etc., may be determined by making a series of duplicated assays, taking care to produce lead buttons of approximately the same weight. The silver prills from the first assays are weighed and the average taken. These are wrapped in pure lead foil of the same weight as the button to be cupelled, and used as checks in the cupellation of the next series of lead buttons, and the average gain or loss deducted from or added to the weight of silver found. This is, however, seldom done. *E.g.* First cupellation yielded prills averaging 0.0263 grm. These used as checks gave prills averaging 0.0259 grm., showing a loss of 0.0004 grm., which

was added to the amount found with second series of assays (see also below).

NOTE.—A series of alloys for cupellation, containing 0.5, 1.0, and 2.5 per cent. of silver respectively, should be made and cupelled in 5 grms. lots of 4 each. They are best made from pure lead (made by reducing red lead with charcoal alone) and pure silver reduced from silver chloride. Both may be rolled out into strips, cut fine, and the required quantities weighed out, mixed and melted in a carbon crucible covered with a charcoal plug. About 25 grms. of each alloy should be made. After cupellation calculate percentage loss on silver present. A further series of alloys, each containing the same weight of silver, but varying weights of lead, may be made and cupelled to ascertain the influence of the quantity of lead.

The following table, from "Crooke's Select Methods," coincides with the author's experience, except that perhaps the losses given are slightly in excess of those actually found, when the assay is free from copper and carefully conducted at the lowest temperature.

The results may be summed up as follows. With a constant weight of lead the loss in silver increases with the silver present, but the percentage calculated as the weight of the silver is greater as the silver prill diminishes in size.

The presence of refractory oxides, for the complete liquefaction of which higher temperatures must be maintained, causes an increase in the loss of silver by absorption.

Actual percentage of silver found by assay.			Cupellation loss or percentage of silver to be added to the actual percentage found by assay in order to show the true percentage of silver contained in the assay, the lead in or added to the assay being the following multiples of the silver present.									
			1	2	3	4	5	6	8	11	18	16
99.75	}	...	0.25	0.32	0.39	0.45	0.5	—	—	—	—	—
99.50			0.22	0.29	0.36	0.42	0.47	0.69	0.83	—	—	—
90	0.20	0.26	0.33	0.39	0.44	0.64	0.75	—	—	—
80	0.18	0.23	0.29	0.35	0.40	0.58	0.68	0.82	—	—
70	0.16	0.20	0.26	0.30	0.36	0.52	0.61	0.74	—	—
60	0.14	0.17	0.23	0.26	0.32	0.46	0.54	0.65	—	—
50	0.12	0.15	0.20	0.22	0.27	0.39	0.46	0.55	0.62	—
40	0.11	0.13	0.18	0.18	0.25	0.36	0.42	0.50	0.57	—
35	0.10	0.12	0.16	0.16	0.22	0.32	0.38	0.45	0.51	—
30	0.09	0.10	0.14	0.14	0.20	0.29	0.34	0.40	0.45	—
25	0.08	0.09	0.12	0.12	0.17	0.25	0.29	0.35	0.39	0.45
20	0.07	0.08	0.10	0.11	0.15	0.20	0.23	0.28	0.32	0.37
15	0.06	0.07	0.09	0.10	0.13	0.17	0.19	0.23	0.26	0.32
12	0.05	0.06	0.08	0.09	0.11	0.15	0.17	0.20	0.23	0.27
10	0.04	0.05	0.07	0.08	0.10	0.14	0.16	0.18	0.21	0.25
9	0.03	0.04	0.06	0.07	0.09	0.13	0.15	0.16	0.18	0.22
8	0.02	0.03	0.05	0.06	0.08	0.12	0.13	0.14	0.16	0.20
7	0.01	0.02	0.04	0.05	0.07	0.10	0.11	0.12	0.14	0.17
6	—	0.01	0.03	0.04	0.06	0.09	0.10	0.11	0.12	0.14
5	—	—	0.02	0.03	0.05	0.07	0.08	0.09	0.10	0.11
4	—	—	0.01	0.02	0.04	0.05	0.06	0.07	0.08	0.09
3	—	—	—	0.01	0.03	0.04	0.04	0.05	0.06	0.07
2	—	—	—	—	0.01	0.03	0.03	0.04	0.04	0.05
1	—	—	—	—	0.01	0.03	0.03	0.04	0.04	0.05

In ordinary assaying, ores, etc., no correction is made for loss, but for bullion and rich products correction is essential.

Concordant results are obtained by working on buttons of lead, of approximately the same weight. 18 to 20 grms. is a convenient size.

For bullion and rich ores the assay must be corrected by reducing the slags (see p. 104), and adding the weight of the prills thus obtained to the main button. The cupellation loss is determined and the assay corrected.

Estimation of Silver in an Ore.—Pot Assay.—Take 25 grms. ore, 35 grms. sodium carbonate, 5 grms. borax, 25 to 40 grms. red lead, and 3 grms. flour, or 8 of argol, the variations being made in accordance with previous considerations. Melt and pour. Powder slag, mix with 20 grms. red lead and 2 grms. flour, and remelt. After cleaning buttons, weigh, cupel separately, and weigh prills of silver obtained. If necessary, make corrections for loss, and calculate to ounces of silver per ton, thus—

Ore taken	25	grms.
Weight of first button of lead	21	"
„ second button of lead	12.5	"
„ silver obtained	0.2356	grm.
„ „ from slag button	0.0235	"
Total silver found	0.2591	"
Deduct silver in red lead	0.001	"
Silver in ore	0.2581	"

$$\text{Percentage of silver found } \frac{0.2581}{25} \times 100 = 1.032.$$

From table cupellation loss, a

$$1 \text{ per cent. silver alloy with 16 times lead} = 0.05$$

$$\text{Corrected result per cent.} \quad \dots \quad 1.0824$$

To calculate ounces per ton from percentage found. From the percentage find lbs. per ton, thus—

$$100 : 2240 :: 1.0824 = \frac{1.0824}{100} \times 2240 = 24.24576$$

Or, multiply the percentage by 22.4.

These are avoirdupois lbs. per English ton. The American ton is only 2000 lbs.

To convert avoirdupois pounds to troy ounces :

$$\begin{aligned} 1 \text{ lb. avoirdupois} &= 7000 \text{ grns.} \\ 1 \text{ oz. troy} &= 480 \text{ ,,} \\ \therefore 24 \cdot 2457 \times \frac{7000}{480} &= 353 \cdot 58 \text{ ozs.} \end{aligned}$$

Or, the pounds may be multiplied by 14·5833.

Or, the number of ounces per ton of 2240 lbs. may be obtained directly by multiplying the percentage by 326·666, or by 291·666, for ton of 2000 lbs.

Scorification Assay.—Proceed as directed (p. 106). Clean the slags by fusion in a crucible with red lead and flour as before. Weigh and cupel the buttons.

Weight of ore taken	5 grms.
„ lead used	60 „
Silver contents of lead	...	100 grms.	= 0·008 grm. silver.
Weight of silver found	0·0520 grm.
„ „ from slag	0·0047 „
Total silver found	0·0567 „
Deduct silver in lead used	0·0048 „
Silver in ore	0·0519 „
Percentage of silver found	$\frac{0 \cdot 0519}{5} \times 100 = 1 \cdot 038$		
Cupellation loss (from table)	0·05 „
Corrected result per cent.	1·088 „

Calculate ounces per ton, as in previous example.

To convert decimals of an ounce into pennyweights and grains, multiply by 20 and point off, and then multiply decimal remainder by 24; thus—

$$\begin{aligned} 10 \cdot 884 \text{ troy ounces} &= 10 + \cdot 884 \times 20 = 7 \cdot 680 = 10 \text{ ozs. } 7 \cdot 680 \times 24 = \\ &16 \cdot 32 \text{ grns.} = 10 \text{ ozs. } 7 \text{ dwts. } 16 \cdot 32 \text{ grns.} \end{aligned}$$

ASSAY TABLE.

Bullion per cent.	Long Ton, 2240 lbs.	Short Ton, 2000 lbs.	Bullion per cent.	Long Ton, 2240 lbs.	Short Ton, 2000 lbs.
	ozs. dwts. grs.	ozs. dwts. grs.		ozs. dwts. grs.	ozs. dwts. grs.
0·0001	0 0 15·6	0 0 14	0·07	22 17 8	20 8 8
0·0002	0 1 7·3	0 1 4	0·08	26 2 16	23 6 16
0·0003	0 1 23	0 1 18	0·09	29 8 0	26 5 0
0·0004	0 2 14·7	0 2 8	0·1	32 13 8	29 3 8
0·0005	0 3 6·4	0 2 22	0·2	65 6 16	58 6 16
0·0006	0 3 22	0 3 12	0·3	98 0 0	87 10 0
0·0007	0 4 13·7	0 4 2	0·4	130 13 8	116 13 8
0·0008	0 5 5·4	0 4 16	0·5	163 6 16	145 16 16
0·0009	0 5 21	0 5 6	0·6	196 0 0	175 0 0
0·001	0 6 12·8	0 5 20	0·7	228 13 8	204 3 8
0·002	0 13 1·6	0 11 16	0·8	261 6 16	233 6 16
0·003	0 19 14·4	0 17 12	0·9	294 0 0	262 10 0
0·004	1 6 3·2	1 3 8	1·0	326 16 8	291 13 8
0·005	1 12 16	1 9 4	2·0	653 12 16	583 6 16
0·006	1 19 4·8	1 15 0	3·0	980 9 0	875 0 0
0·007	2 5 17·6	2 0 20	4·0	1307 5 8	1166 13 8
0·008	2 12 6·4	2 6 16	5·0	1634 1 16	1458 6 16
0·009	2 18 19·2	2 12 12	6·0	1960 18 0	1750 0 0
0·01	3 5 8	2 18 8	7·0	2287 14 8	2041 13 8
0·02	6 10 16	5 16 16	8·0	2614 11 4	2333 6 16
0·03	9 16 0	8 15 0	9·0	2941 7 0	2665 0 0
0·04	13 1 8	11 12 8	10·0	3268 3 8	2916 13 8
0·05	16 6 16	14 11 16	11·0	3594 19 16	3208 6 16
0·06	19 12 0	17 10 0	12·0	3921 16 0	3500 0 0

To obtain ozs., dwts., grs. from table—

For long ton—

500 grns. ore give 0·0525 grns.

then per cent. = $\frac{0·0525}{5} = 0·0105$

0·01 = 3 5 8

0·0005 = 0 3 6·4

Hence ore contains 3 8 14·4 per ton (2240 lbs.)

For short ton—

0·01 = 2 18 8

0·0005 = 0 2 22

3 1 6 per ton (2000 lbs.)

Assay of Alloys.—The foreign metals present determine, by their nature and quantity, the amount of lead necessary for their complete removal, and the temperature required. Whether an assay has had the needful amount may be judged by the appearance of the cupel under the prill. This should be light-coloured—yellowish or greenish in tint, showing that lead (or bismuth) was the last metal

to remain with the silver, sufficient litharge having been formed at the last to wash the cupel under the button. If the copper has not been entirely removed the button will adhere strongly to the cupel.

The amount of lead necessary to effect the complete absorption of copper as oxide is between 16 and 17 times the weight of copper present. Silver has, however, considerable protective action on copper during cupellation, and prevents its oxidation. An alloy containing 50 per cent. of silver requires the use of the same amount of lead as pure copper, although no increase need be made for poorer alloys. It is this protective action which causes the quantity of lead used for alloys containing little copper to be comparatively so great.

Gold exerts an even greater protective action than silver, and twice the above proportion of lead is required in cupelling gold-copper alloys. Platinum has a like effect.

Alloys containing per- centage of copper.	Times weight of lead required.	Proportion of copper to lead.
0 ...	1
5 ...	4 ...	1:80
10 ...	7 ...	1:70
15 ...	9 ...	1:60
20 ...	10 ...	1:50
30 ...	12 ...	1:40
40 ...	14 ...	1:35
50 and over ...	16-17 ...	1:32

Cobalt, nickel, iron, zinc, tin, and antimony are removed at the beginning of the cupellation, but, if in large quantity, the oxides are not dissolved by the litharge and absorbed by the cupel. The conditions necessary for complete absorption are :—the amount of lead oxide formed on the exposed surface shall be sufficient to dissolve the refractory oxide simultaneously formed, and the temperature must be sufficiently high. Hence, in the cupellation of very impure leads, the temperature at the outset should be considerably higher than that at which the operation is continued, in order to prevent the assay freezing.* Nickel gives a brownish black colour. Iron gives a black or reddish-black colour, and scoræ; zinc, a yellowish-white incrustation; tin, a greyish encrusting mass; antimony, an orange ring, with cracking of the cupel, if the amount be large. Copper, on the other hand, being less oxidizable than lead, remains to

* Hence cupellation always causes more trouble at the commencement than afterwards. Towards the end pure litharge, or litharge mixed with oxide of copper, is formed. The latter mixture, if sufficient litharge be present, is very fluid and readily absorbed.

the end, and thus becoming concentrated, exerts its worst effect on the rapidly diminishing button. Buttons which retain copper, because too little lead has been used, invariably yield low results, owing to the increased absorption of silver.

In cupelling impure buttons and alloys, better results are obtained by maintaining a temperature somewhat higher than is necessary with silver-lead buttons (see p. 113).

1. **Substances to which cupellation may be directly applied—**

- (a) **Lead and bismuth alloys.**—Argentiferous lead and bismuth.
- (b) **Silver** (pure or nearly pure).—Native and bar silver, retorted amalgam, silver alloys, with gold, copper, and platinum.
- (c) **Argentiferous copper alloys.**—Native copper, tough pitch copper, and (copper) coins; copper precipitate.

The substances under (c) require so much lead for direct cupellation that they should always be first scorified.

2. **Substances which do not yield good results by direct cupellation—**

- (a) **Ores of silver and argentiferous compounds.**
- (b) **Impure copper and copper alloys.**—Bottoms and black copper, brass (zinciferous alloys), bronze (stanniferous alloys), German silver.
- (c) **Antimonial alloys.**—Type metal, Britannia metal.
- (d) **Zinc alloys.**—Brass, Parkes' crusts, pattern alloys, etc.
- (e) **Telluric ores and products.**
- (f) **Nickel and iron alloys.**—Cast iron, bears, nickel, cupronickel, etc.
- (g) **Tin alloys.**—Solder, pewter, and Britannia metal, bell metal, gun metal, and bronzes.
- (h) **Argentiferous residues.**—Sweep, residues, substances containing silver bromide chloride or iodide, litharge, and other oxides.

In the assay of alloys by cupellation, a trial assay should always be made, and the appearance of the cupel noted. If any infusible scorix be formed, or any cracking of the cupel takes place, the metal should first be scorified with more lead than is required for its direct cupellation, and the scorification continued till the lead button is soft and malleable.

If tin or antimony be present, more than one scorification will probably be necessary. In this case it is better to add at once the quantity of lead necessary, and scorify (see p. 108, charges for scorification).

Assay of Silver Amalgam.—Five grammes of the amalgam are

weighed out, placed on a cupel in a muffle at a very dull red heat, and heated cautiously for an hour. When all the mercury has been expelled, 25 grms. of lead are added and cupelled. In some cases it is better to remove the cupels, wrap the residual silver in the lead, and place on a fresh cupel.

Assay of Bullion.—Base bullion includes argentiferous lead or copper, and other metals carrying a considerable proportion of silver. Lead, if sufficiently rich and pure, is cupelled direct, from 5 to 20 grms. being taken. If impure or poor, the sample is scorified alone, or if very impure, with an addition of lead free from silver, and the resulting button cupelled. Copper and its alloys are treated by scorification, followed by cupellation (see table, p. 108). Copper alloys, rich in silver, and commercial silver are cupelled direct. It has already been remarked that losses invariably occur during the process. There is no doubt that in some cases lead is retained by the silver, occasionally as much as 1 per cent. Tables of correction for the losses in cupellation have been framed, but, as the loss is variable, and depends on so many factors, they are unreliable. The only satisfactory method, if tables are to be used, is for each operator to prepare his own. The better plan is to check the accuracy of the assays by cupelling at the same time a number of test samples similar in character to the assays, containing a weighed quantity of pure silver, about equal in weight to that in the assay proper, the gain or loss in weight of which is added to or deducted from the result of the assays. These checks should be inserted at the ends of the rows of cupels. One will serve for two rows if placed midway between them. A preliminary assay is made of 2.5 grs. or 0.25 gm., with 50 grs. or 5 grms. of pure lead, and the result weighed. Suppose the preliminary assay of a bar has shown its richness to be approximately 800 fine or 80 per cent. of silver, with copper only as impurity. In the exact assay 10 grs. or 1 gm. of the alloy is weighed and cupelled with the necessary lead (see p. 118). Beside it a test, made up of 8 grs. of pure silver and 2 copper, or 0.8 gm. silver and 0.2 gm. copper, is cupelled with the same quantity of lead. The results are weighed. If the pure silver has lost weight, the assay may be assumed to have sustained a similar loss, and an addition must be made. If a gain has occurred, a deduction must be made from the result of the assay. Except in the valuation of bullion, this method is seldom resorted to.

In reporting in ounces and pennyweights, "better" or "worse" than standard silver, it is easier to employ special weights. 12 grs. = 1 lb., with subdivisions into dwts., grs., etc.

SILVER.

121

The student, for practice, should make alloys containing—

92·5 per cent. silver 7·5 copper

90 " " 10 "

80 " " 20 "

Melt in carbon crucibles, and cupel them against checks of pure silver.

WET ASSAY OF SILVER.

THE metal is easily separated from other metals except lead by taking advantage of the insolubility of its chloride in water and weak acids, and the readiness with which the precipitate collects and subsides on heating and shaking.

The solution is prepared in the case of alloys by treating with nitric acid (sp. gr., 1.2). All alloys, except those containing a large percentage of gold or platinum, are completely decomposed, and the silver passes into solution. If tin or antimony be present it remains as an insoluble oxide, which may retain traces of silver. The solution is diluted, any insoluble matter filtered off, washed, and the silver precipitated from the solution.

In dealing with ores, the finely powdered material is digested with nitric acid till completely decomposed, and hydrochloric acid then added till the action ceases. The solution is evaporated nearly to dryness in a beaker, the residue taken up by warming with a little hydrochloric acid, and diluted considerably. The insoluble residue contains all the silver as chloride, which is filtered off and washed. The silver chloride is dissolved out by treating it with weak ammonia on the filter. This is continued till no cloudiness appears on acidifying the last portions of the filtrate with nitric acid. The filtrate is acidified with nitric acid, and the reprecipitated chloride collected, dried, and weighed.

This method is not adopted for silver ores unless of great richness. Sometimes ores are treated with acids to remove foreign metals, which would interfere with dry assay. In that case, instead of dissolving out the chloride with ammonia, the whole of the insoluble residue is treated by pot assay, or by scorification (see also p. 307).

Assay of Alloys.—English Mint Method for Coinage and Silver Bullion. The silver is precipitated as chloride by a standard solution of common salt. The chloride is caused to cohere by shaking vigorously, and in consequence settles rapidly. After standing a few minutes to clear, half a milligram of silver can be detected in 150 c.c. of liquid. To ensure accuracy it requires the presence of a constant quantity of silver in the assay solution.

Standard Salt Solution.—(a) 5.127 grms. of pure common salt are dissolved and made up to a litre (at 15° C.). 1 c.c. = 0.01 silver.

Weaker Standard Solution of Salt.—100 c.c. of (a) are diluted to 1 litre. 1 c.c. = 0.001 silver.

Weak Standard Silver.—1 grm. of pure silver is dissolved in nitric acid (sp. gr. 1.2) and diluted to a litre at 15° C. 1 c.c. = 0.001 silver. The three solutions must be in exact agreement.

It is necessary to know approximately the quantity of silver present in each assay, and a preliminary assay of some sort must be made to approximately determine the fineness. This may be done by cupellation, or by a rough assay conducted on the same lines as the actual assay. The quantity of the alloy containing 1 grm. of silver is then calculated thus—with an alloy 750 fine

$$750 : 1000 :: 1 : Q = \frac{1000}{750} = 1.3333 \text{ grm.}$$

This quantity is accurately weighed out.

In conducting the assay sufficient of the strong salt solution to precipitate a gram. of silver is added at once from a special burette arranged to read to within 0.05 c.c. = half a thousandth (100 c.c. = 1 grm. Ag.). The solution is sometimes weighed instead of being measured. The assay is thoroughly shaken and allowed to settle bright and clear. The titration is finished by running in the weak solution from a burette half a c.c. at a time, shaking between each addition, till no turbidity appears when a fresh addition is made. The last and half the previous addition is deducted, as the whole was unnecessary.

Thus, in an assay of nearly pure silver, the equivalent of 99.55 c.c. of the strong solution was added. An additional 3.5 c.c. of the weak solution was necessary before precipitation was complete. Deducting the last and half the previous addition (0.75 c.c.), 2.75 c.c. was really required.

$$\begin{aligned} 99.55 \times 0.01 &= 0.9955 \\ 2.75 \times 0.001 &= 0.00275 \\ &0.99825 \text{ silver} \\ &= 998.25 \text{ parts per thousand.} \end{aligned}$$

If the assay be a little poorer than was anticipated, the first addition of salt will more than precipitate the silver. In that case, addition of the weak solution will produce no precipitation. The procedure is then reversed, and the weak solution of silver nitrate is added from a burette until a faint precipitate is produced, half the last addition and sufficient to precipitate the *weak* salt solution added being deducted as before.

As the solution varies in volume with the temperature, its expansion

must be allowed for if the accuracy of the work demands it. A table of expansion is given below—

	°C.	grms. silver.		°C.	grm. silver.
100 cc. @	4	= 1.000989	100 cc. @	15	= 1.000
	5	= 1.001398		16	= 0.99991
	6	= 1.001598		17	= 0.99979
	7	= 1.001898		18	= 0.99966
	8	= 1.002098		19	= 0.99954
	9	= 1.002098		20	= 0.99940
	10	= 1.001898		21	= 0.99922
	11	= 1.001698		22	= 0.99902
	12	= 1.001498		23	= 0.99884
	13	= 1.00109		24	= 0.99865
	14	= 1.000069		25	= 0.99845

It will be observed that, if the solution be made and standardized at 15° C., 100 c.c. at 15° will exactly precipitate 1 gram. of silver: at other temperatures more or less silver will be precipitated. At 20° only 0.99940 gram. will be precipitated, and if 1 gram. of silver be present, more than 100 c.c. salt solution will be necessary to precipitate it completely. At temperatures below 15°, 100 c.c. will precipitate more silver. When the standard solutions are weighed, no corrections are necessary.

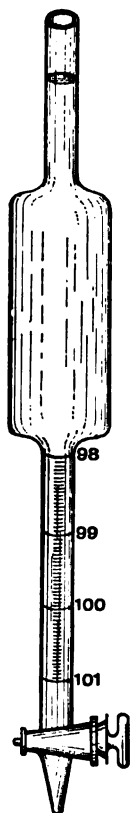


Fig. 68.

The apparatus best suited for measuring the solution is a tap-pipette, shown in Fig. 68. The upper stem is marked for filling, and the delivery tube is graduated from 98–101 c.c. in 0.05 divisions. When bought, the accuracy of the burette should be tested by weighing it, filled to the mark with distilled water, at 15° C. 100 c.c. should then be allowed to run out, and the burette again weighed. The difference should be 99.9125 grms. If not correct, the burette should be rejected, or the error determined and noted. The bottles in which the assay is made should be of thin, clear white glass, about 8-oz. capacity, with well-ground, flat-topped stoppers.

Standardizing the solutions.—Dissolve 1 gram. pure silver in 10 c.c. nitric acid (sp. gr. 1.22) in one of the bottles in a water-bath, or by very gentle heat on the hot plate. Expel the nitrous fumes, and without shaking add about 10 c.c. water. Then add 100 c.c. of the strong salt solution from the burette, taking care that it runs directly into the bottle, and not down the side. Wet the stopper, then insert it, shake vigorously for a couple of minutes, and stand aside to settle.

Fill two ordinary burettes, (1) with the weak solution of salt, (2) with the weak silver nitrate solution.

When the solution in the bottle is clear, cautiously add 0.5 c.c. of the weak salt solution, and observe the upper layer of the liquid in the bottle to see if a turbidity is produced. If so, shake, and let settle. Then add another 0.5 c.c., shake, and stand aside, and repeat till no further turbidity results. When, on an addition being made, no precipitate forms, neglect that addition and deduct half the previous one.

If, on the first addition of weak salt solution no precipitate results, the standard solution is too strong. To ascertain its strength, proceed as follows: Add 0.5 c.c. of the weak silver nitrate to neutralize the 0.5 c.c. salt added, and, after shaking and settling, proceed with the addition of silver nitrate instead of common salt as before. If the solution be correct, no precipitate will be formed by the weak salt solution or by the silver nitrate after neutralizing the weak salt solution first added.

100 c.c. salt.	
+	-
+	

It is well to put a paper, divided as shown, beside the assay, and mark each addition by a plus sign on the left for salt, and a minus sign on the right for silver, to avoid mistakes.

Calculation and Correction.—Suppose, after adding the 100 c.c. salt, five additions, = 2.5 c.c., of the weak salt solution are necessary, the sixth producing no precipitate, deduct 0.25 (half the last) $2.5 - 0.25 = 2.25 = 0.00225$ grm. silver, then 100 c.c. of the stronger salt solution = 1 grm. — $0.00225 = 0.99775$.

The solution may be used with this knowledge, or made up to normal strength by adding from a strong salt solution, the strength of which is known, sufficient to make each c.c. = 0.01, *i.e.* 100 c.c. = 1 grm. Suppose 50 c.c. of this strong salt solution = 1 grm. of silver—

$$100 \text{ c.c.} = 2 \text{ grms. silver}$$

$$1 \text{ ,,} = 0.02 \text{ ,,} \quad \textit{i.e.} \text{ } 0.01 \text{ grm. in excess of requirement.}$$

Then since 100 c.c. of the standard solution is 0.00225 deficient, 1 litre (1000 c.c.) will be 0.0225 short, and the amount of the strong solution to be added per litre may be calculated thus:—

$$\frac{0.0225}{0.01} = 2.25 \text{ c.c. to be added per litre of standard.}$$

$$\text{Then } 1000 \text{ c.c.} \times 0.0099775 = 9.9775$$

$$2.25 \times 0.02 = 0.0450$$

$$\text{Total silver equivalent of } 1002.25 \text{ c.c.} = \underline{10.0225}$$

$$\frac{10.0225}{1002.25} = 0.01 \text{ of silver per c.c.} = 1 \text{ grm. per } 100 \text{ c.c.}$$

After this addition a further determination should be made to test its accuracy. When absolutely corrected the stock solution should be carefully preserved. The Winchester or carboy containing the solution should be provided with means of agitating the contents before drawing off to ensure uniformity, and preserved at an even temperature. The solution should be removed by means of a syphon, a narrow air tube should pass down to the bottom of the bottle, and a set of nitrogen bulbs filled with water should be attached to the open end.

The weaker solution is made as required, 100 c.c. of the stronger solution being diluted with distilled water to 1 litre.

Assay of a Coin or Bullion.—It is necessary to know the approximate fineness of the sample before proceeding. This may be determined by a cupellation assay, or a rapid preliminary determination. As nearly as possible, a constant weight of silver is taken in all cases. This is usually 10 grs. or 1 grm., according to the weights used. Suppose the rough assay shows 96.3 per cent., or 963 thousandths, then, $\frac{1000}{963} \times 1000$ would be taken = 1038 mgrms., 1.038 grm. In practice, however, so as to deal with no weights less than multiples of 5 mgrms. 1040 mgrms. would be taken. If the alloy showed 727 thousandths of silver, $\frac{1000}{727} \times 1000 = 1375.5$ mgrms., 1375 mgrms. would be taken for the assay.

The quantity required must be weighed out accurately, and placed in one of the stoppered bottles. 10 c.c. of nitric acid of specific gravity 1.2 are added, and the bottle placed on the hot plate, or in a water-bath, till the metal is dissolved. Expel all nitrous fumes, and cool. The volume should not be less than 10 c.c. Then add from the burette (pipette) exactly 100 c.c. of the strong salt solution (noting the temperature and correcting as per table). Observe the pipette to see the exact amount that has been added. It may vary from the correct quantity by half a thousandth or more. Shake till the precipitate settles quickly. When the supernatant liquor is clear, add 0.5 c.c. of the weak salt solution, and observe whether a cloudiness is produced. If so, add another 0.5 c.c., shake well, let settle, and repeat, shaking after the

addition of each 0.5 c.c. till no further precipitation results. The amount of solution added will be 100 c.c. (corrected as shown) plus the weak solution used (with the necessary deductions). Thus, to a sample weighing 1375 mgrms. approximately 727 fine, 100 c.c. of the strong standard solution was added, but on examination of the burette the delivery was seen to have been faulty and only 99.95 had been delivered. The temperature of the laboratory was 20°, and the standardizing had been conducted at 15° C. By reference to table—

$$100 \text{ c.c. at } 20^\circ = 0.9994 \text{ grm.}$$

$$\therefore 99.95 = \frac{0.9994}{100} \times \frac{99.95}{1} = 0.9989 \text{ grm.}$$

To the solution nine additions of 1 c.c. each of the weaker solution were necessary. Deduct the last, as it produced no turbidity, and half the former, as it was not all required,

$$= 0.008 - 0.0005 = 0.0075.$$

hence, $0.9989 + 0.0075 = 1.0064$ mgrm. of silver present in 1.375,

$$\text{fineness, therefore,} = \frac{1.0064}{1.375} \times 1000 = 731.91.$$

If the first addition of weak salt solution produces no cloudiness, add from another burette an exactly equivalent amount (0.5 or 1.0 c.c.) of the weak silver nitrate solution to neutralize it. Shake, and let settle. Then proceed with subsequent additions of silver nitrate exactly as in the former case, but, in calculating, deduct the silver (after neutralization of the weak salt solution) added, from the equivalent of the 100 c.c. of standard solution.

Thus, if 1375 mgrms. of the sample, as above, took 100 c.c. of the standard strong solution, and 7 c.c. of the silver nitrate solution were added, one of which was necessary to neutralize the 1 c.c. of weak salt solution and the last produced no precipitate, and half the last but one was unnecessary, assuming the temperature to be 15° C., 100 c.c. = 1 grm. silver.

Deduct silver equivalent of—

$$7 \text{ c.c., less } 2.5 \text{ c.c.} = 4.5 \text{ c.c.} = 0.0045 \text{ grm.}$$

$$\therefore \text{sample contains } 1 - 0.0045 = 0.9955 \text{ grm. silver.}$$

$$\text{and fineness} = 1000 \times \frac{0.9955}{1.375} = 724 \text{ thousandths.}$$

Indian Mint Assay.—"Chloride" process.—In the Indian mint the chloride is precipitated, collected in a special manner without filtration, and weighed. Although the method is unlikely to commend itself to

European workers, a short account is necessary, as showing modified methods of manipulation due to different conditions. The difficulty of keeping solutions of constant strength, the presence of mercury, lead, etc., in the bullion, and the necessity of a preliminary assay are assigned as reasons for the changes made.

The weighed samples, each 18.825 grs., are transferred to the dissolving bottles, and $1\frac{1}{2}$ drm. of nitric acid, of sp. gr. 1.2, added to each. The bottles are placed in a water or sand bath, provided with a stand for the stoppers, which are removed. If the metal be impure, a stronger acid (sp. gr. 1.32) is employed. After solution, 6 ozs. of cold distilled water are added. Then, without shaking, $1\frac{1}{2}$ drm. of hydrochloric acid, sp. gr. 1.06 is added to each from a pipette. After standing 5 minutes, the stoppers—moistened with distilled water—are put in, and the bottles shaken vigorously for 2 or 3 minutes, till the chloride becomes curdy and settles rapidly. Any particles on the side are washed down by swirling the liquid round the bottle, and distilled water is added till the bottles are nearly full. The bottles are allowed to rest four hours, when the clear liquor is removed by a syphon or a pipette. Distilled water is added, and the precipitate gently agitated with a circular motion, the sides washed down if necessary, allowed to settle for two hours, and the liquor again drawn off. If necessary, for example, when the silver is coarse or lead is present, a third or fourth washing is resorted to. The bottles are filled with water and gently laid on their sides to cause the chloride to collect in one spot. The chloride is removed by inverting the bottles over small numbered cups, $1\frac{1}{2}$ inch wide and $1\frac{1}{2}$ inch high, standing in saucers 4 inches in diameter, in a pneumatic trough filled with water. This is effected by removing the stopper, covering the neck by the thumb, and lowering it into one of the cups, before removing the thumb. Most of the chloride falls at once into the cup, and any adherent particles may be caused to fall by gentle tapping or shaking. The trough is provided with divided rings, into which the bottle is slipped and thus supported. When the chloride has fallen, the bottle is removed and carefully examined. No particles should remain, nor should any fall into the saucer if deftly manipulated.

The cup with the precipitate is removed, about half the water carefully decanted, and the precipitate broken up with a thick rounded glass rod, the end of which is afterwards rinsed into the cup.

After removing the water, the precipitate is dried gradually, first in an air or steam bath at 100° C., and subsequently at 150–175° C. in an air-bath or on a hot plate. The chloride is weighed by lifting it by the forceps from the cup on to the loose pan of the balance. It is sufficiently tough and hard to admit of this.

Gold in this assay is valued as silver remaining undissolved after treatment with nitric acid.

The bottles used must have flat bottoms (inside) and conical tapering sides. They are about $6\frac{1}{2}$ inches high, and $2\frac{1}{2}$ inches in diameter at bottom, and have a capacity of 11 to 12 ozs.

The use of special weights obviates all calculations, as in many other cases. 18.825 grs. of pure silver yields 25 of chloride. The weights are therefore marked as follows :—

Value of weight in grs.	Marked.			
25.0 "	...	1000.00	fineness, in thousandths.	
22.910 "	...	918.66	"	"
22.5 "	...	900.00	"	"
and so on to 0.025 "	...	1.00	"	"

VOLHARD'S PROCESS.

The silver is precipitated in a strongly nitric acid solution by potassium sulphocyanate. Excess of the reagent is indicated by means of iron alum, which gives an immediate and deep red colour with excess.

The salt employed must be free from chlorides.

Standard Solution of Potassium Sulphocyanate.—9.7 grms. of the pure salt is weighed, dissolved in water, and diluted to one litre.

Iron Alum Solution.—A saturated solution is employed. Some undissolved crystals should be left at the bottom of the bottle.

Standardizing.—Weigh out 0.5 grm. pure silver, dissolve in 10 c.c. nitric acid, sp. gr. 1.2, in a 300 c.c. flask, and boil off all nitrous fumes. Dilute to 100 c.c. with cold distilled water, add 5 c.c. of the iron alum solution, and shake.

Run in the sulphocyanide solution cautiously from the burette. A whitish precipitate is thrown down, attended by a red coloration, which in the earlier stages disappears immediately, but as the finishing point is neared, only on shaking. The precipitate collects in flocks, and the liquid clears rapidly as the end is approached. Generally at the end the liquid becomes quite limpid. When nearing this point the reagent is added drop by drop till a faint brownish red coloration is produced, which does not disappear on shaking.

As far as possible all conditions (amount of free acid, temperature, amount of iron salt, volume) should be kept constant. The principal points to be observed are the amount of free acid and iron salt and freedom from nitrous acid (which destroys the colour).

The titration should be done cold, and the strength of the sulphocyanate carefully noted on the bottle. The solution does not alter on keeping, and is best diluted, so that 1 c.c. = 0.01 grm. silver.

The Assay.—Proceed exactly as for standardizing.

Limits of Application.—Metals, like mercury and palladium, which are precipitated by sulphocyanate, vitiate the results. Copper in large quantities (over 60 per cent.) gives trouble, as immediately the silver is completely precipitated black cupric sulphocyanate is thrown down, and masks the end reaction. In dealing with coppery alloys a weaker solution may be employed with advantage, and should be run in slowly.

Coloured salts of nickel and cobalt mask the final reaction, but by practice the end can be readily recognized, especially if recourse be had to titrating back with standard silver nitrate.

Lead, zinc, manganese, iron, cadmium, arsenic, antimony, tin, bismuth do not interfere.

Treatment of Silver Residues.—**Reduction with Zinc.**—Wash the residues well with water, and finally with dilute hydrochloric acid. Place some zinc rods among the chloride, and leave in contact in a warm place till completely reduced. Remove the zinc; wash with hot water. Digest the residue with hydrochloric acid (1 part acid, 1 water) for some hours. Wash and collect the silver, and melt down at bright redness under a flux consisting of 10 parts sodium carbonate and 1 part nitre— $2\text{AgCl} + \text{Zn} = \text{ZnCl}_2 + \text{Ag}_2$. The silver obtained by this process from pure chloride is practically pure.

Reduction with Chalk and Charcoal—(Guy Lussac's method). The chloride is dried, ground, and mixed as follows :—

Silver chloride, 100 parts; chalk, 70 parts; charcoal, 4·5 parts.

The charge, thoroughly mixed, is heated in a deep crucible, which should not be more than two-thirds full, to a very bright red heat. Much gas is evolved, and care must be taken that the contents do not boil over.

The reaction is—



The oxychloride fuses well, but if at all pasty, a little common salt and borax may be added.

Silver prepared in this way is not pure. Stas found iron and silicon in the metal prepared from pure chloride. It may be purified by heating to bright redness under a flux of sodium carbonate and nitre.

Reduction with Sodium Carbonate, or with sodium and potassium carbonates.—The chloride is fused with from one to four times its weight of carbonate of soda or a mixture of equal parts of carbonates

of soda and potash. For pure chloride its own weight is sufficient, especially if potassium carbonate or a little nitre is also present. When less pure, more flux must be employed.

DETERMINATION OF SILVER IN EXTRACTION WORKS

In dry crushing silver mills and leaching works it is necessary to determine the proportion of silver existing as chloride in the pulp in order to control the operations. The method employed follows the actual process closely. A solution of sodium thiosulphate of about 20 per cent. strength (200 grms. per litre) and a solution of sulphide of soda are required.

The total silver in the pulp is first determined by scorification and cupellation, as per page 106, on from $\frac{1}{10}$ to $\frac{1}{2}$ an assay ton, *i.e.* from 2·9166 grms. to 14·583 grms. (2000 lbs. = 1 short ton).

A second sample is treated with thiosulphate solution, allowed to settle, and the clear liquor decanted through a filter. This is repeated till the filtrate is not darkened by the addition of sodium sulphide. The pulp is then transferred to the filter, washed with hot water, dried, and it and the paper containing it ignited, and the pulp and paper ash assayed by scorification and cupellation.

The difference in the results of the first and second assays is due to the silver chloride removed by the treatment with thiosulphate.

Similar methods working on the lines of the processes are employed for the Ziervogel (sulphate), Russell,* and similar processes.

The suitability of an ore for treatment by thiosulphate processes may be ascertained as follows :—

Russell Tests.—The material is ground to pass a 30 mesh sieve, and the ore assayed in the raw state, and after roasting with salt (7–15 per cent. salt). After leaching the roasted ore with thiosulphate of soda (hypo) and “extra” solutions, the residue is assayed for silver and the silver in the liquor precipitated by sulphide of soda.

The total silver is estimated in the raw ore by scorification and cupellation.

The “hypo” and copper sulphate are made into 20 per cent. solutions, *i.e.* 200 grms. per litre. The following charges are from Dagget, The Russell process. Trans. A.I.M.E.

Several portions of $\frac{1}{2}$ assay ton (14·583 grms.) are weighed out, put into 300 c.c. beakers, and treated as follows :—

* The “extra” solution used in the Russell process is cuprous thiosulphate. This is formed when copper sulphate is added to a solution containing thiosulphate of soda.

1. **Raw Ore and Tailings.**—(a) Add 150 c.c. water and 100 c.c. hypo. Let stand 12 to 16 hours, cold. Decant; add 25 c.c. CuSO_4 , dilute to 300. Stand 12 hours; add 20 grms. hypo (dry). Stand 12 to 16 hours, cold, filter, and wash.

(b) Add 150 c.c. water, 100 c.c. hypo. Stand 12 to 16 hours; add 20 grms. hypo and 25 c.c. CuSO_4 . Stand 12 to 16 hours, cold, filter, and wash.

(c) 100 c.c. cold water, 25 c.c. CuSO_4 . Stand 1 hour; add 100 c.c. water, 100 c.c. hypo, heat to 55°C . (130°F .), filter, and wash.

(d) 250 c.c. cold water and 25 c.c. CuSO_4 . Stand 1 hour, cold; add 20 grms. hypo, heated to 55°C . Decant. Repeat a second time, filter, and wash.

(e) Add 200 c.c. cold water and 90 c.c. CuSO_4 . Stand $\frac{1}{2}$ hour; add 90 grms. hypo, heat to 55°C ., filter, and wash.

(f) Add 250 c.c. cold water, 25 c.c. CuSO_4 , heat to 55°C ., and decant. Add 20 grms. hypo and 25 c.c. CuSO_4 , dilute to 300 c.c., heat, filter, and wash.

Roasted and Chloridized Ore, Mattes, and Tailings.—*Test (a)* Add 50 c.c. water and 25 c.c. CuSO_4 . Stand 2 hours, dilute to 200 c.c.; add 20 grms. hypo. Stand 2 hours, filter, and wash. All cold.

(b) Add 250 c.c. water and 25 c.c. CuSO_4 . Stand 12 to 18 hours; add 20 grms. hypo. Stand 12 to 18 hours, filter, and wash. All cold.

(c) Repeat (b), allowing to stand for 2 hours only.

(d) Wash well with cold water, then add 25 c.c. CuSO_4 , dilute to 300 c.c. Stand 12 to 18 hours; add 20 grms. hypo, filter, and wash with hot hypo, and filter.

(e) No washing. Add 250 c.c. cold water and 25 c.c. CuSO_4 . Stand 1 hour; add 20 grms. hypo, heat to 55°C . Decant. Repeat, then filter, and wash.

(f) Wash with hot water, add 200 c.c. hot water and 90 c.c. CuSO_4 . Stand $\frac{1}{2}$ hour; add 90 grms. hypo, heat to 55°C ., filter, and wash.

(g) Wash with hot water, add 90 c.c. CuSO_4 . Stand $\frac{1}{2}$ hour; add 90 grms. hypo, dilute to 300 c.c., heat to 55°C ., filter, and wash.

(h) Wash with hot water, add 20 grms. hypo and 50 c.c. water. Stand 1 hour; add 25 c.c. CuSO_4 , dilute to 300 c.c., heat to 55°C ., filter, and wash.

The above experiments indicate the methods of testing adopted to prove the suitability of an ore for treatment.

Assay of Claudet Liquors containing silver chloride in solution.—A measured quantity of the liquor, usually half a gallon, is taken in the dipping jug. To this is added excess of hydrochloric acid, 3 grms. of potassium iodide, and 100 grms. of lead acetate, and 1 grm. of lamp

black. The precipitate is collected on a large filter (a folded filter is best), dried, coarsely ground, and mixed with 50 grms. sodium carbonate (or soda ash) and 4 grms. borax, and run down in a crucible at a low red heat.

The button of lead obtained is cleaned and cupelled in the ordinary manner.

Assay of Hard Lead.—From 25 to 50 grms. of the lead is taken, an equal weight of assay lead added, and scorified till the slag covers the button, small additions of borax glass being made. This is poured, and the lead tested. If still hard, further scorification, with more lead, is resorted to. When soft, the button is cupelled and the prill weighed.

Assay of Zinc crusts or argentiferous Zinc.—This is best done by dissolving the sample, 5 to 10 grms., in dilute sulphuric acid (sp. gr. 1.4). This leaves most of the silver and lead insoluble. A little hydrochloric acid is then added to insure the complete precipitation of the silver, and the liquid decanted or filtered. The residue is washed and dried. It is then either assayed by scorification and cupellation, or run down in a pot, and the button of lead cupelled.

Scorification.—This is only applicable when little silver chloride is present. The residue, after drying and burning the filter paper, is mixed with $\frac{1}{2}$ grm. of carbonate of soda, and afterwards with the necessary amounts of granulated lead and borax. The weight of assay lead necessary varies with the amount of the residue, but should amount to ten times its weight. The borax ordinarily should be about 1 grm. When scorification is complete, the contents of the scorifier may be poured or allowed to cool, and the button broken out. Cupellation is effected in the ordinary manner.

Pot Method.—The residue is mixed with 10 grms. of sodium carbonate, then 25 grms. red lead, 0.75 grm. of charcoal, and 4 grms. of borax, and run down.

The resulting button is tested and cupelled.

The reason for adopting dry assay in such cases is that the lead present would interfere with wet methods.

GOLD.

SUBSTANCES in which the metal has ordinarily to be determined.

I. Ores.

- (a) Gold ores, containing metallic gold in a matrix of quartz, with or without oxides of other metals.
- (b) Ores containing gold in quartz matrix, with the sulphides, etc., of other heavy metals.
- (c) Ores containing tellurium.
- (d) Auriferous ores of other metals, consisting mainly of sulphides, arsenides, etc.

II. Reguli, mattes, and speiss.

III. Slags.

IV. Sweep and other residues.

V. Alloys.

- (a) With silver,—all crude gold, native gold, retorted amalgam, electrum.
- (b) Silver and copper,—jewellery and coinage alloys.
- (c) Copper,—tough pitch, bottoms and black copper.
- (d) Bronze and brass.
- (e) Platinum and lead.

VI. Precipitated gold—from chlorination and cyanide processes.

VII. Silver mud from Claudet process.

I. Gold Ores.—(a) Auriferous quartz containing metallic gold in fine or coarse particles or as thin leaves. Frequently the gold in the general body of the quartz is quite invisible, although selected samples may show it. The appearance of the quartz is very variable, and it is almost impossible to lay down any general rules for the recognition of gold-bearing quartz either by colour or any easily recognizable appearances. As a rule, however, quartz containing hydrated oxide of iron resulting from the decomposition of iron pyrites is likely to be auriferous, and particles of gold will frequently be found interspersed in the oxide, which should be carefully scanned with a magnifying glass.

- (b) Highly mineralized quartz, *i.e.* quartz containing ores of other

metals, especially sulphides and arsenides of iron, is also likely to be auriferous. It may be observed that auriferous belts are most likely to be found in regions in which manganiferous, cobaltiferous, and bismuthic minerals are found. In highly mineralized quartz free gold often occurs, in addition to the gold contained in the sulphides, etc.

Telluride Ores—Many of the telluride minerals contain gold in large quantity.

Native Tellurium occurs crystallized, in hexagonal forms, also massive and granular; colour, tin white; lustre, metallic; brittle; hardness, 2-2.5; sp. gr., 6.1-6.3; composition, tellurium with gold and iron, seldom more than three per cent. of gold being present.

Sylvanite.—Graphic tellurium, cryst. form, monoclinic, often arranged in regular lines, like arabic characters, also massive and granular; colour, steel grey to silver white or yellowish; streak, same; lustre, metallic; hardness, 1.5-2; sp. gr., 5.7-8.28; composition, telluride of gold and silver $(\text{AgAu})\text{Te}_2$.

Black Tellurium.—Nagyagite, cryst. form, tetragonal, also foliated and massive; colour and streak, dark lead grey; lustre, metallic to submetallic; opaque, sectile; hardness, 1-1.5; sp. gr., 6.8-7.2; composition $(\text{AuPb})_2(\text{TeSSb})_2$. It contains from 6-20 per cent. of gold.

Tetradymite.—Telluric bismuth, cryst. form, hexagonal, also massive, granular and foliated; cleavage, basal, very perfect; colour, pale steel grey; lustre, metallic-splendent; hardness, 1; marks paper; composition, Bi_2Te_3 .

Telluride minerals when heated in an open tube give a white sublimate which melts to yellowish drops, but becomes white again on solidifying.

For testing gold ores for tellurium, Kustel recommends the following process. The powdered ore is placed in a capsule, and triturated with a little water and mercury. A little sodium amalgam is then added, and if tellurium be present the water acquires a violet colour, which he states to be due to the formation of sodium telluride. If sulphur be present, the water blackens silver foil. If iron sulphide be present, the black precipitate produced may mask the colour, but on pouring off the water, and adding fresh water and a little more amalgam, the tellurium will be found.

II. Ores of other metals are frequently auriferous, the precious metal passing into the metallic products of smelting. It is consequently found in regulus, matte, and speiss.

III. Slags.—These have frequently to be examined to estimate the gold, or ensure their freedom from the precious metal.

IV. (a) Residues containing metallic gold, from users of goldleaf,

jewellers' filings and dust, sweepings, etc., containing earthy and other impurities, and often organic matter, such as paper, leather, etc., which must first be thoroughly burnt off before proceeding with the assay.

(b) Gold melting crucibles or bullion pots.

Native Alloys.—Palladium gold (AuPd). Rhodium gold (AuRh), gold amalgam.

REACTIONS AND TESTS FOR GOLD.

The metal is unattacked by the common mineral acids singly, but dissolves in aqua regia owing to the liberation of free chlorine thus :—



the chloride, AuCl₃, being formed.

Gold is attacked and rendered soluble by free chlorine, bromine, iodine (in solution), potassium cyanide, and kindred substances under suitable conditions.

A solution of chloride of gold gives the following tests :—

1. Sulphuretted hydrogen gives a black precipitate of Au₂S₃, soluble in ammonium sulphide, reprecipitated by acids. Au₂S₃ is insoluble in nitric acid.

2. Ferrous sulphate produces a brownish black precipitate of metallic gold, which becomes bright on rubbing or heating.



3. Oxalic acid, sulphur dioxide, sulphites, and other reducing agents precipitate gold.

4. Stannous chloride produces a purplish brown precipitate known as "purple of cassius," of varying composition. When freshly precipitated the precipitate is soluble in ammonia. This reaction is very sensitive.

5. Copper or zinc placed in the solution precipitates the metal.

6. If a Swedish filter paper be moistened with a solution of gold chloride, and, after drying, burnt, the ash, instead of being white, is tinged with pink or purple.

Dry Reactions.—Before the blowpipe gold fuses to a brilliant yellow globule, which does not oxidize. The bead is malleable, and insoluble in nitric acid.

Detection of Gold in Minerals.—1. In minerals containing visible gold the metal may be distinguished from—

(a) Iron and copper pyrites, and similar bodies, by its softness and malleability. The former is too hard to scratch with a knife, while the latter crumbles. It also yields a yellow shining metallic streak, whereas both these minerals yield a dark grey, almost black, streak. It is

fusible, and no fumes of sulphur dioxide are observable when heated before the blowpipe.

(b) Yellow mica, by not being sectile. If the specks are too small to test, some of the stone should be crushed and carefully washed, to remove the earthy matters, the residue mixed with carbonate of soda, and fused on charcoal. If a bead remains, it may be tested with nitric acid. If not, the cavity in the charcoal is cut out, and the portion removed, crushed carefully, and washed. The specks of gold are collected and run down with lead on a small cupel before the blowpipe and cupelled.

2. In minerals in which the gold is not visible.

(a) A quantity of the crushed mineral is moistened with aqua regia and warmed gently. The mass is treated with water, the solution evaporated to small bulk, and tested with stannous chloride.

Pyrites and other sulphurous ores must be roasted prior to treatment with aqua regia. The roasting is assisted by mixing the pyrites with powdered marble or fine sand.

(b) By amalgamating with mercury. 50 grms., or 2 oz. of the ore, are first very finely crushed and thoroughly wetted with water in a mortar. A small quantity of mercury is added and ground with the moist ore for at least ten minutes. The mortar is then sunk under water and the contents carefully washed, so as to remove the finest particles. The residue, consisting of the coarser particles and the mercury, is reground and rewashed till nothing remains but the mercury. This is placed in a porcelain capsule or scorifier, dried with filter paper, and very carefully heated, to remove the mercury. If auriferous, a *film* of gold remains. Much of the mercury may be condensed by inverting a large bowl over the capsule while igniting. If pyrites is being treated, it must first be roasted, and, to save labour in grinding, marble dust is better than sand, with which to mix it.

(c) The finely ground sample is treated with about its own volume of chlorine water, bromine water, or iodine dissolved in potassium iodide, and well agitated for some time. Two or three hours is sufficient for bromine, but iodine should stand at least twelve hours. The solution, after settling, is decanted and evaporated to small bulk (or may be tested direct), and the solution tested with stannous chloride, or by saturating a Swedish filter paper with the solution and burning it. In applying the latter test, the paper is saturated with the liquor and dried. This may be repeated several times. The paper is then burnt and the colour of the ash noted. Bromine and iodine are better than chlorine, as they attack the foreign matters in the ore to a less

extent, owing to a less tendency to form hydrogen salts. The nature of the coloration may be tested by a drop of bromine water. If gold, it disappears.

Ores containing 2 dwts. or more per ton give a good reaction for gold by this test, and poorer ores (down to a few grains) will give a distinct reaction if carefully treated. 100 grms. of ore, containing half a dwt. of gold per ton, gave a distinct reaction on evaporating the filtrate and washings to about 1.5 c.c.

Pyritic ores must be first roasted (with sand), and carefully heated to full redness, to decompose sulphates.

WASHING (PAN) ASSAY FOR SANDS AND GRAVELS.

This assay is worthless as a means of determining the exact quantity of gold present, but is sometimes of value in concentrating the gold in soft gravels and sands, poor in gold, or as a preliminary trial. The washing is done either on a shovel, as in tin assay, a circular dish, or in a vanning bowl or trough (Fig. 69). The trough is 16 ins. long, 7 ins. across in the widest part, and $1\frac{1}{2}$ in. deep.



FIG. 69.

The ore is first finely ground, and a weighed quantity is carefully washed (see directions, tin assay), till the gold is visible. The quantity may be estimated by amalgamating it with mercury, and igniting the amalgam in a small crucible.

AMALGAMATION ASSAY.

This is conducted on a larger sample than the foregoing. A large sample of from 5 to 10 lbs. is taken, dried, crushed, and sifted. Any particles of gold of sensible size which the ore may contain are flattened by the crushing, and will not pass through the sieve. These are known as "metallics" and are assayed separately.

From 500 grms. to 1000 grms. is mixed with water to a stiff paste, in an iron or wedgwood mortar, about a table-spoonful of mercury added, and the whole thoroughly ground for from 20 minutes to 1 hour. Another table-spoonful of mercury is added, and the grinding continued for a further period. The mass is then washed in an enamelled pan, or similar vessel, the amalgam collected and distilled, and the residual gold weighed. No separation of mercury prior to distillation must be attempted. The washing and amalgamation are sometimes done together in the vanning trough, the mercury added being 5 to 10 grms.

In this case the washing must be very slow, or amalgam will be lost. In Arizona a couple of hours are devoted to this washing, and the residual amalgam is washed with potassium cyanide before retorting. The retorted gold is refined by cupellation and parting, and weighed. Generally from 80 to 90 per cent. of the gold present is obtained by these methods.

DRY ASSAY.

The principles underlying the assay of gold are, so far as the pot, scorification, and cupellation processes are concerned, the same as for silver. Procedure which ensures the extraction of the largest proportion of silver will yield the best results with gold (see pp. 101-106).

Gold exerts a much greater protective action than silver in cupellation, especially on copper, and in order to insure the complete removal of that metal, it is necessary to prolong the operation by increasing the proportion of lead. Little difficulty is, however, encountered in assaying ores, as the quantity of gold present is so small, but in assaying alloys, etc., a large increase has to be made in the added lead, both in direct cupellation and scorification assays.

Preparing the Sample.—The sample should be very carefully and systematically taken (see p. 3). This is especially important, owing to the irregular occurrence of the metal in the ore. The sample should weigh not less than 200 grms. The whole must be powdered, and passed through an 80 sieve. If the gold be "coarse," some flattened particles will remain. These are the "metallics," and must be first accurately weighed and assayed separately by scorification and cupellation, an aliquot part of the gold obtained being added to the yield from the portion of the fine material assayed.

Assay of Gold Ore.—1. Concentration of gold by pot or scorification method, with preliminary roasting, if necessary.

- 1a. Scorification of lead buttons.
2. Cupellation.
3. Weighing of prill = gold + silver, platinum, etc.
4. Inquartation (if necessary).
5. Preparation of cornet.
6. Parting with acid, collecting, washing, and drying.
7. Weighing gold. (Gold + silver) - gold = silver.

Pot Assay.—This method is most suitable for poor and earthy or oxidized ores, inasmuch as they can be assayed without preliminary treatment, and larger quantities can be operated on. Ores containing much sulphur, antimony and arsenic, are best "dead roasted" with the

addition of a little coal dust at the close, to reduce sulphates, arsenates, etc., but if the quantity of sulphur be small, as in a mineralized quartz, no roasting is necessary.

If the ore contains sulphides, and is not previously roasted, a preliminary assay, to determine its reducing power, must be made (see silver, p. 105). If sulphides are absent this is unnecessary.

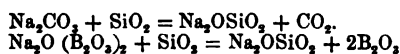
The general conditions attaching to silver assay apply here with equal force. Owing to the smaller proportion of gold usually present, there is some tendency not to get the whole of the gold collected, but this is counterbalanced by the more ready separation and higher specific gravity of gold.

The metal is less volatile than silver, and hence less loss occurs from this cause in cupellation. It has, however, a much greater affinity for and protective action on copper, and hence retains that metal with greater tenacity, necessitating the employment of much larger quantities of lead in cupellation.

Assay of Gold Quartz.—1. Quartz containing no pyrites, and little oxide of iron.

Here it is only necessary to flux the silica, and reduce lead in sufficient quantity to concentrate the gold.

One part of silica is fluxed by about $1\frac{1}{2}$ parts of dry sodium carbonate, or about $3\frac{1}{2}$ of borax.



In the latter case the boric anhydride liberated can combine with and flux earthy matters or metallic oxides, and as quartz is seldom quite free from these, a little borax is always added.

An excellent mixture for pot assay for rich ores—

300 grs. or 20 grms. of powdered ore.				
450	„	30	„	red lead or litharge.
450	„	30	„	sodium carbonate.
75	„	5	„	borax.
15	„	1	„	lampblack or 30 grs. or 2 grms. of flour or starch.

For poor ores two or more such charges may be mixed separately, and the buttons of lead scorified together (see p. 106), and finally cupelled. Or a larger quantity of ore may be taken, and the fluxes increased in proportion. The quantity of reducing agent is not increased.

The mixture is put into a crucible, and treated in the same manner as a silver ore (p. 101). The final heating should be intense, to thoroughly liquefy the slag and enable the reduced lead to collect. If

the slag is pasty, an addition of borax with prolonged heating will generally render it fluid.

The button is freed from slag and carefully prepared, as in silver assay, and finally cupelled (see below).

Assay of Pyritous Ores, and ores containing metallic sulphides.—These may be dealt with in two ways. The raw ore may be assayed directly, or it may be previously roasted to expel the sulphur, etc. In the latter case it is treated like a quartz containing no pyrites, but much oxide of iron.

When treated directly, it is necessary to first determine the reducing effect of the ore itself, 5 grms. of ore mixed with 50 grms. of red lead or litharge, whichever it is intended to use (red lead is best for sulphurized ores), and 5 grms. of carbonate of soda, and heated. The resulting button is weighed. The weight of the button obtained determines whether it is necessary to diminish the quantity of charcoal or other reducing agent added, or to employ nitre to diminish the amount of lead reduced.

The charge is made up as follows :—

300 grs. or	20 grms. of ore.	
450 „	30 „	red lead.
300 „	20 „	carbonate of soda.
45 to 60 „	3 to 4 „	borax.

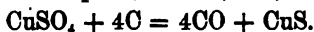
With the necessary quantity of reducing agent or addition of nitre as indicated by the trial assay to produce a button weighing 20–25 grms.

For poor ores more than one fusion must be made, and the buttons scorified together as before indicated.

Effect of Pyrites and other Sulphides.—Besides influencing the amount of lead reduced, sulphides, when treated without roasting, may cause loss of gold by the formation of fusible double sulphides and oxy-sulphides, which escape reduction, and carry silver and possibly gold with them into the slag. If arsenic or antimony is present, arsenates or antimonates may be formed and cause loss of silver in the slags.

Such ores are best dealt with by roasting off the sulphur and arsenic prior to reduction. This may be done on a roasting dish in a muffle first at a low temperature, and afterwards at full redness. If more convenient, an iron shovel may be used heated over a fire; the shovel should be coated with milk of lime, whiting, or red ochre to prevent the ore sticking. The roasting must be conducted slowly, to avoid mechanical loss in the vapours passing off. Care must be taken not to fuse the ore. The roasting should be continued till all smell of sulphur dioxide has disappeared, and then a little charcoal, coal dust, or anthracite

should be well mixed in, and completely roasted off with strong heat, so as to decompose by reduction, sulphates, arsenates, and antimonates formed, and allow all the sulphur, arsenic, etc., to be removed; *e.g.*—



The roasted ore is then treated as below.

Assay of Gold Quartz containing much oxide of iron or other earthy matter, and roasted pyritical ores.

In this case the only difficulty arises in fluxing the oxide of iron.

The following mixture yields good results:—

300 grs. or	20 grms. of ore or roasted product.
750 „	50 „ litharge.
225 „	15 „ carbonate of soda.
120 to 150 „	8 to 10 „ borax.
35 „	1.75 „ charcoal, or 200 grms. or 10 grms. of argol.

Use a No. 5 pot, and heat the assay slowly. The button should weigh about 20 grms. If it is much less, it is due to ferric and other peroxides in the ore, and the assay must be repeated, with a proportionately larger amount of reducing agent, making at the same time any variation in the amount of fluxes which may be deemed desirable.

General Remarks.—The loss of gold in the pot assay is less than the loss in assaying silver, and considerable variations may be made in the charges without vitiating the result as regards the gold. If it is intended, as is generally the case, to determine both silver and gold, which commonly occur in the same mineral, the assay should be conducted with all the precautions taken in the case of silver. This refers both to the treatment in the crucible and on the cupel.

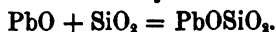
Scorification Assay for Gold.—This method is only suitable for the assay of rich materials, as the large quantities, which must necessarily be taken when the ores are poor, would involve the use of too many dishes, too much lead, and occupy too much time, while the results for such ores are, if anything, lower than those obtained by pot assay.

In general the methods followed for the scorification of silver ores will serve also for gold ores, but usually a larger proportion of borax is employed. The method is specially suitable for cuprous ores, and has the advantage that, with the exception of nickel speiss, and certain metallic admixtures,* it is unnecessary to calcine the ore before assay. It is also unnecessary to make any preliminary assay.

Assay of Quartzose Ores containing little pyrites.—From eight to ten parts of lead are necessary to furnish litharge to flux the quartz and

* Finely divided material containing much copper, iron, nickel, or tin.

leave sufficient lead for cupellation. Each part of silica requires approximately a minimum of $3\frac{2}{3}$ its weight of litharge, or $3\frac{1}{3}$ times its weight of lead, to flux it satisfactorily.



It is better to exceed this, so that the excess may act as a solvent on any small quantities of metallic oxides present, especially those of antimony, tin, and copper.

Take 50 grs. or 5 grms. of the prepared ore and 450 grs. or 45 grms. of granulated lead. Divide the lead into two parts. Mix one-half with the ore and place on a $2\frac{1}{2}$ -inch scorifier. Cover the assay with the other half of the test lead, and scorify as for silver. If the ores are poor, four such scorifiers must be prepared, and the resulting buttons scorified together (see silver, p. 109). It is best to add a little glass borax about 5-7.5 grs. or 0.5-0.75 gm. at the end of the scorification during the final heating, to secure perfect liquidity of the slag. The contents are poured into a mould, or the scorifiers are allowed to cool, and broken.

Assay of Galena.—Since, on roasting, galena oxide of lead is formed, which serves as a flux, less test lead is necessary.

Take 50 grs. or 5 grms. of the ore, 5 to 6 times its weight of lead, and 7.5 grs. or 0.75 gm. borax, and proceed as before. The borax should be added after the roasting stage is complete. Some assayers mix it with the ore and the first half of the lead.

Assay of Auriferous Antimonial Ores (Stibnite, Kermesite, Bournonite, etc.).—The important points to be observed in the assay of these substances are, to have sufficient lead to combine and form antimonate with the antimony that is not removed during the roasting stage of the operation, and sufficient lead oxide and borax to produce fluidity of slags, otherwise a refractory ring of red antimoniate of lead forms round the scorifier. The final temperature must be high, but during the roasting stage a low temperature gives best results, as there is less mechanical loss in the fumes given off by the assay. The latter does not apply with the same force to alloys or ores that have been previously roasted.

Take 50 grs. or 5 grms. of ore, 16 times its weight of test lead, and from half to its own weight of borax. The whole of the latter should not be mixed with the assay at first, but added in portions, (1) on mixing, (2) when roasting is complete, (3) when giving final heating.

Assay of Arsenical Ores.—These are treated in the same way as antimonial ores, except that less borax is employed as the arsenic roasts off. When nickel and cobalt are present the larger proportion of borax should be used.

Take 50 grs. or 5 grms. of ore, 16 times its weight of test lead, and from $\frac{1}{2}$ to $\frac{1}{2}$ its weight of borax, and proceed as above.

Assay of Fahlers.—Take 17 times its weight of test lead, and $\frac{1}{10}$ to $\frac{1}{2}$ of its weight of borax.

Assay of Iron and Copper Pyrites and Zinc Blende.—These require 12 to 15 times their weight of test lead, according to amount and nature of gangue, and from $\frac{1}{10}$ to $\frac{1}{2}$ of their weight of borax. The samples containing least-quartz require the increased weights of lead.

Assay of Basic Ores.—Dolomites, Gossans, calcareous and clayey ores, Kaolinite, etc.—These require from 8 to 10 times their weight of lead, and from $\frac{1}{4}$ to their own weight of borax, which may be added at once, or in small portions at a time, as advised under anti-monial ores.

General Observations.—The period of roasting, fusion, scorification, and final fusion succeed each other in the same order as in silver scorification. In the roasting stage the heat should be moderated, to prevent loss of precious metals in the vapours expelled. The final heating should be intense, and the scorification stage hot enough for the slag to clear readily.

Where much borax is used it should, as recommended above, be added in several portions, or so much slag will be formed in the earlier stages of the operation as to cover the button and arrest the scorification.

Cupellation.—This operation is conducted in the same manner as cupellation for silver. There is, however, less liability for gold to be lost either by absorption or volatilization, and consequently a somewhat higher temperature may be employed without danger. It is, in fact, advisable in cupelling buttons containing copper to urge the furnace somewhat, as this metal clings much more tenaciously to gold than to silver, as will be observed from the quantities of test lead to be employed in the cupellation of alloys (see p. 148). Buttons containing tin and antimony must be scorified with more lead, in order to remove those metals, prior to cupellation.

The button obtained contains, of course, the silver present in the sample. As any alloy of gold and silver containing less than 30 per cent. of gold is white, a yellow prill is evidence that it contains more than that amount.

Gold buttons are not liable to spit, but on cooling exhibit the peculiar phenomenon of suddenly flashing out brightly when a certain temperature has been reached, at the same time appearing greenish. The prills are cleaned and weighed.

Methods of dealing with poor Ores.—It is best, where possible, to deal with a sufficient quantity of the ore to obtain a weighable button,

but the following alternative course may be pursued. A small weighed quantity of pure gold, not exceeding 1 grain in weight, may be added to the cupellation, and a similar quantity of gold wrapped up in pure lead of the same weight as the assay button, cupelled side by side with the assay. The resulting buttons are weighed, and the excess gives the gold (and silver, if any) in the sample. It is, of course, necessary to "part" the button obtained in order to ascertain this (see below).

INQUARTATION AND PARTING.

The separation of gold from silver, for assay purposes, is effected by boiling the alloy with nitric acid. The alloy should contain not less than 75 per cent. of silver. If the prill is yellow, weigh out, approximately, $2\frac{1}{2}$ to 3 times its weight of pure silver, wrap the prill with the silver in a fragment of thin sheet lead, at least equal in weight to the two metals. Drop it on a heated cupel, and remove the lead by cupellation. Flatten the button, wrapped in paper, on a smooth anvil, anneal it by heating to redness, and, if large enough, roll out into a ribbon (if not large enough to handle in this way, flatten carefully on the anvil). Anneal the strip, and, if large enough, coil it up round a pencil, or thin glass rod, into a "cornet."

The cornet is then placed in a test-tube $5 \times \frac{5}{8}$ inches, and 2 c.c. of nitric acid (sp. gr. 1.26) consisting of equal parts of pure nitric acid and distilled water, added and warmed gently. The silver is rapidly dissolved, and the gold is left as a brown or purplish brown powder, or flaky residue. Larger prills are treated in parting flasks, using more acid.

The solution is carefully decanted, and a few drops of stronger nitric acid added and gently warmed, to remove the last traces of silver. The residual gold is then washed by decantation, great care being exercised to avoid loss, and collected as follows:—

The test-tube is filled brimful of distilled water, and a weighed porcelain crucible inverted on the top. By means of the forefinger of the left hand this is held in position, and the tube and crucible are rapidly inverted. No liquid is lost, and the heavy gold quickly falls into the crucible. To remove the tube, it is best to immerse the crucible in a deep white porcelain dish (to render any particles which might possibly escape plainly visible), and carefully lift the tube over the edge of the crucible and slide it off under water. The water in the crucible is then decanted, and the crucible dried, heated to about 250°C ., cooled on a desiccator, and weighed.

Some assayers, for convenience, remove the powdery gold from the

crucible, place it in a scrap of sheet lead, and cupel it into a prill. The chances of loss are, of course, greater when this is done.

NOTE.—The washing must be carefully and completely done, and no hesitation must occur in inverting the crucible. Care must be taken, in placing it under water, that the inrush of the water does not wash out any particles of gold.

The assay of metallic and native gold must be conducted as for assay of gold alloys.

Influence of Platinum, etc.—In ores containing platinum, that metal is left with the gold and silver after cupellation. It seriously interferes with that operation, and renders the removal of copper specially difficult. The complete removal of copper from an alloy of gold, platinum, and copper, is almost impossible, as the platinum causes the retention of metallic copper in the prill. This action is reduced by alloying with silver, thus diluting the alloy, and by cupelling at a high temperature in order to facilitate the ready solution of the copper oxide formed in the molten litharge. At the higher temperature less lead is necessary, and the loss of silver is actually less than when working with more lead at lower temperatures. Buttons of gold and silver containing platinum (even if in very small quantity) exhibit a crystalline appearance on the surface, and have a dull, very slightly yellowish or grey tinge. If the cupellation is completed at the necessary high temperature the edges are well rounded, but the “passing” (*i.e.* the coloured bands, circular motion, etc.) is slower and less strongly marked. When the assay is not hot enough, the button is flat.

In parting, the platinum dissolves out with the silver, unless it exceeds 7 per cent. of the alloy. The resulting solution is yellowish or straw-coloured. See Platinum.

Calculation of Results.—In whatever denominations the weighings are made (grains, grams, or otherwise), the number of ounces per ton may be reckoned thus—

$$\frac{\text{weight of prill}}{\text{weight of ore taken}} \times 100 = \text{percentage of gold.}$$

$$\frac{\text{percentage of gold}}{100} \times 2240 = \text{lbs. per ton (avoirdupois).}$$

$$\text{lbs. per ton} \times \frac{7000}{480} = \text{troy ozs. per ton.}$$

$$\text{or the percentage} \times 326.6 = \text{ozs. per long ton (2240 lbs.).}$$

$$\text{the percentage} \times 291.6 = \text{ozs. per short ton (2000 lbs.).}$$

NOTE.—2240 lbs. = 1 ton (English), 2000 lbs. = 1 ton (American), 7000 grs. = 1 lb. (avoir.), 480 grs. = 1 oz. troy.

Or the amount may be determined by reference to tables (see p. 117).

ASSAY OF GOLD ALLOYS.

THE fineness of gold alloys is usually expressed in carats and carat grains.*

Touchstone Assay.—This is only an approximate method of determining the carat fineness of an alloy. It is conducted by means of a set of needles containing known proportions of gold. These are rubbed on a hard black surface so as to leave a metallic streak which is treated with acid. The sample to be tested is dealt with in a similar manner, and by comparison with the results obtained from the standard needles its fineness is determined.

Four or five sets of needles, in which the gold is alloyed in different ways, are necessary.

(a) Copper-gold (red); (b) silver-gold (white); (c) silver-copper gold, the alloy being equal parts silver and copper; (d) silver-copper-gold, the alloy being two parts silver and one copper; (e) silver-copper-gold, the alloy being one part silver and two parts copper.

Each set contains about thirty needles, which differ from each other by half a carat, beginning at about four carats. The touchstone is a close-grained, hard, flinty, black or very dark slate; but a bit of black wedgwood basalt ware answers equally well.

The acids used are pure nitric acid, and a "test" acid consisting of a mixture of 98 parts of pure nitric acid (sp. gr. 1.34), and 2 parts hydrochloric acid (sp. gr. 1.17). (Or 98 parts pure nitric acid (sp. gr. 1.434), and 2 parts strong hydrochloric acid, and 25 parts water.) Nitric acid does not act on gold over 15 carats fine, or the test acid on gold over 18 carats. In using the needles, the series to which the alloy to be examined belongs is first determined by observation, and the set of needles nearest in colour selected.

The surface of the article to be examined is filed, or otherwise removed, or the determination may be worthless, owing to plating, or to "colouring," a process by which goldsmiths enrich the surface by treatment with solvents in order to remove part of the alloy. A clean streak

* 1 carat = $\frac{1000}{24}$ = 41.6 parts per thousand.

is then made on the touchstone, and on this a drop of pure nitric acid is placed, by means of a glass rod. It is allowed to act for a few seconds and then wiped off with a soft cloth, to see whether the streak remains unaltered. If unattacked the test acid is employed. By careful comparison of the effects with those produced on streaks from the needles an experienced man can approximately judge the fineness of the alloy, but it is impossible to ensure accuracy. This method serves for gold plate, etc., for valuation purposes.

Cupellation Assay (see also p. 109).—Most of the gold alloys that have to be assayed contain only gold, silver, and copper. In such cases direct cupellation is all that is necessary.

In cases where other metals are present, *e.g.* nickel zinc, etc., preliminary scorification is necessary. This is conducted on the same lines as for silver (p. 106).

The quantity of lead necessary to completely remove copper from gold at ordinary cupellation temperature is as follows :—

Gold.	Copper.	Approx. carat fineness.	Lead required.			
950 ...	50 ...	23-22 ...	10 times weight of sample.			
900 ...	100 ...	21½ ...	12	"	"	"
875 ...	125 ...	21 ...	14	"	"	"
800 ...	200 ...	20 ...	16	"	"	"
750 ...	250 ...	18 ...	20	"	"	"
625 ...	375 ...	15 ...	24	"	"	"
500 ...	500 ...	12 ...	28	"	"	"
500-0 ...	1000-500 ...	0-12 ...	34	"	"	"

10 grs., or 0·5 grm., 12 grs., or 0·6 grm., are taken, according to fineness. See statement of results.

The sample is wrapped in the necessary amount of sheet assay lead, and dropped into a red-hot cupel, and the cupellation carried on for the removal of the copper, etc. Enough pure silver is then weighed out to make, with that present in the alloy, the total silver equal to about three times the amount of gold. This is wrapped with the gold in a little sheet lead (about twice its weight) and cupelled.

If excess of silver is present, more accurate results can be obtained by adding fine gold so that the prill contains 25 per cent. gold.

The inquarted button is then flattened on an anvil, annealed by heating to redness, and rolled into a ribbon about 1½ inch long, and ⅓ inch wide. This is again annealed and coiled round a thin glass rod into a "cornet."

When the determination of silver is unnecessary, as in the assay of jewellery alloys for stamping purposes, one cupellation will suffice, and in these cases, the weighed sample is placed in a little pocket of sheet lead with 2½ times its weight of fine silver, and placed on

a heated cupel, the alloying with silver and removal of the copper being thus simultaneously effected. A convenient plan is to have alloys of lead and fine silver, ready made in such proportions that the necessary amount of lead contains the required amount of silver, several such alloys being kept on hand, ready weighed out and made up into pockets, to suit varying qualities of gold. Such alloys may be made by melting the quantities of lead necessary for cupelling the various alloys with $2\frac{1}{2}$ parts of fine silver in a carbon crucible. The lead should be cut up, and mixed with the silver and the whole melted rapidly, poured into a flat ingot mould, cooled quickly, and rolled out. This should then be weighed off, an addition to the quantities given above, of $2\frac{1}{2}$ parts being made for the silver, and folded into pockets ready for use. Thus, for a 15-carat alloy, melt 24 parts lead, and $2\frac{1}{2}$ silver and from the resulting sheet, cut $26\frac{1}{2}$ times the weight of the samples used. If 0.5 grm. is the ordinary weight of assay pieces, take 13.25 grms. approximately of the argentiferous lead, *i.e.* (26.5×0.5).

Parting.—This is done in a parting flask (Fig. 44) or in a matrass—

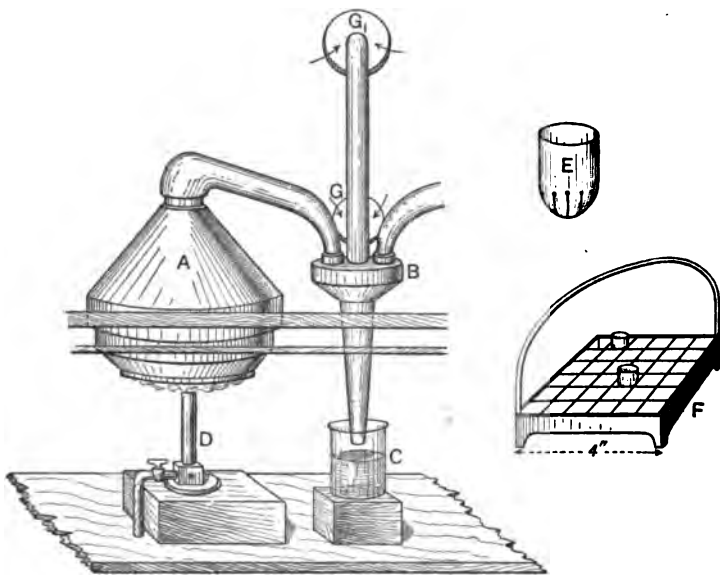


FIG. 70.

a glass parting-bulb, with a long neck holding about 90–100 c.c. The cornet is placed in the flask, about 50 c.c. of nitric acid, sp. gr. 1.16 (2 parts water, 1 acid), added and heated by immersion in boiling water till action ceases. The solution is then poured off (and reserved), and

about 30–35 c.c. of acid, sp. gr. 1.26 (equal parts acid and water), added, and heated in boiling water for about 10 minutes. This is repeated. The flasks or matrasses should be inclined during both operations to prevent the projection of particles from the mouth. The second acid is poured off, and the gold is well washed by decantation, care being taken not to break up the gold. The flask or matrass is next filled brimful with water, and the mouth covered by a parting crucible. On inversion the gold falls into the crucible in a coherent form, and after carefully removing the flask and pouring off the liquid the cornet may be dried and heated to dull redness, and if coherent and firm lifted into the pan of the assay balance, and weighed. If the silver proportion has not been properly adjusted, the cornet may break up. In that case the gold is carefully brushed out on to a watch-glass, or cupelled into a prill for weighing.

Where many assays are done, as at Goldsmiths' Hall and other assay offices, other methods of conducting the parting process are sometimes adopted.

The flask or matrass has been replaced by other apparatus, the cornets being placed in test-tubes with slits cut across the bottom, or in platinum thimbles. These are placed in a tray or perforated plate, and immersed in the acid contained in a flat porcelain dish or platinum boiler. When solution is complete the rack or tray is lifted out, the acid drains away, and the gold washed by immersion in water. It is, of course, necessary in such cases for the gold to remain in a coherent form, and hence that the adjustment of the silver shall be carefully made. Fig. 70 shows such a boiler of platinum with tray and thimble. A is a platinum boiler, 8 inches in diameter, with a funnel-shaped cover, in which the acid is placed; B is a condenser, from which the acid evaporated falls into the beaker, C; D is a Bunsen burner; G, G₁, holes communicating with a flue by which fumes are carried off; F is a divided platinum tray, and E one of the thimbles. These are $\frac{5}{8}$ inch in diameter and $\frac{7}{8}$ inch deep. They are numbered to correspond with the divisions of the cupellation trays on which the prills are first received. Such a method can only be followed when the alloy is such that breaking up does not occur, and is consequently restricted to the assay of coinage and jewellery alloys of approximately known values.

Surcharge.—Generally a trace of silver remains with the gold, but occasionally there is some slight loss, presumably owing to the solvent action of nitrous acid or the presence of impurities in the acid.

To determine this, it is usual to pass a number of check assays through the muffle, as follows: Pure gold equal in weight to the estimated

gold in the samples to be assayed is wrapped up with copper and silver to produce a similar alloy to that under examination, and cupelled with lead in the same manner as the sample. The buttons obtained are inquarted and parted in the same way, and the loss or gain added to or deducted from the weights obtained in the actual assay.

The final weighing may be conducted with the special "gold" weights, or, if samples of 12 grs. are taken, the result multiplied by 2 gives the carat fineness. If 0.6 grm. is taken, the result must be multiplied by 40 ($0.6 \times 40 = 24$). To state the fineness in thousandths the result from 10 grs., or 0.5 grm., may be multiplied by 100 or 2000 respectively.

Assay of Gold Bullion.—The bullion is scorified with lead and the button cupelled, weights similar to those employed for alloys being employed. It is necessary, however, in this case to cupel first with lead alone, and examine the character of the button before proceeding to inquart and part. For effects of platinum, etc., see p. 146.

Value of Bullion.—This is reported in money value per ton. In America ores are also reported in the same manner. Generally the amount of gold is also stated.

Value of gold per troy ounce.

	£	s.	d.	
1 oz. pure gold	=	4	4	11.454 = \$20.39
1 dwt. "	=	0	4	2.95 = 1.02
1 gr. "	=	0	0	2.12 = .0424
1 oz. 22 carat	=	3	17	10.5 = 18.69
" 18 "	=	3	3	8.59 = 15.29
" 15 "	=	2	13	1.159 = 12.74
" 9 "	=	1	11	10.295 = 7.64

TABLE OF RELATIVE VALUES.

In the statement of fineness by carats, etc., it is assumed that 1 lb. of the alloy is taken, and with British assayers the alloy is stated as being so much "better" or "worse" than the standard coinage alloy (22 carat), which contains 11 ozs. 10 dwts. of fine gold, and 10 dwts. of alloy per lb.*

Assay pound	Carats.	Carat gra.	Eighths.	Excess gra.	Decimal equivalent.
1	= 24	= 96	= 768	= 5760	= 1000.0
	1	= 4	= 32	= 240	= 41.6
		1	= 8	= 60	= 10.416
			1	= 7.5	= 1.3021
				0.1	= 0.1736

From this table the value of any alloy can be determined. Supposing it has been made in "thousandths," 41.6 thousandths = 1 carat, and it is a matter of easy reduction.

* Roberts Austen.

Example.—Suppose the fineness of an alloy = 857·6 thousandths, then—

$$\begin{array}{r}
 \frac{857\cdot6}{41\cdot6} = \frac{857\frac{1}{2}}{41\frac{1}{2}} = \frac{\frac{4288}{5}}{\frac{125}{8}} = \frac{12864}{625} \\
 \\
 = 20\cdot5824 \text{ carats} \\
 \quad \frac{4}{8} \text{ " grs.} \\
 \quad \frac{2\cdot3296}{8} \text{ " eighths} \\
 \quad \frac{2\cdot6368}{7\cdot5} \text{ grs.} \\
 \quad \frac{31840}{44576} \\
 \quad \frac{4\cdot77600}{} \\
 \\
 = 20 \text{ ct.} \quad 2 \text{ ct. grs.} \quad 2 \text{ eighths} \quad 4\cdot776 \text{ excess grs.} \\
 \text{or } 1 \text{ " } \quad 1 \text{ " } \quad 6 \text{ " } \quad \text{"worse" than standard gold.}
 \end{array}$$

The excess grains in all cases represent gold in *excess* of the *declared* value.

Assay of Gold and Silver in Copper Mattes.—Four portions of 50 grs., or 2·5 grms., are weighed out, and each mixed with 20 grms. of granulated lead and $\frac{1}{2}$ grm. of borax, placed on scorifiers, and covered with 20 grms. granulated lead and $\frac{1}{2}$ grm. borax. The scorification is conducted at a low temperature at first, and carried further than usual. After pouring, two buttons are placed together, with 40 grms. of test lead and $\frac{1}{2}$ grm. borax, and rescorified down to about 20 grms. The resulting buttons should be malleable and free from copper. After cupellation, the inquarting (if necessary) and parting are carried out in the usual way. The assay should be corrected by running down the slags and cupels.

In some smelting works 10 charges are taken, and the buttons separately cupelled. The resulting buttons are weighed and parted together. The cupels and slags are remelted in lots of two, and the resulting 5 buttons cupelled. The weight of the 5 prills is added to the original weight.

Combined Wet and Dry Method.—25 grms. of the matte in a finely divided state are shaken into a beaker containing 150 c.c. of nitric acid, sp. gr. 1·14, 2 parts water to 1 part strong acid. The liquor is gently heated and more strong nitric added as required till decomposition is complete. The solution should not contain a large excess of free nitric acid. Much of the sulphur will be floating about in a flocculent form. It should be yellowish, showing that the copper compounds are dissolved. If much acid has been used the excess must be removed by evaporation. The liquid is diluted to 500 c.c., and 5 c.c. of sulphuric acid and 10 c.c. of a saturated solution of lead

acetate are added. The lead sulphate formed carries down the finely divided gold. It is filtered off, dried, and placed on a scorifier in the muffle. After the paper has burnt, 50 grms. of test lead are added, and the residue scorified. The resulting button is cupelled. With rich mattes—yielding more than 4 or 5 mgrms. of gold in 25 grms.—a little salt solution must be added to precipitate sufficient silver (as chloride) to avoid inquartation. In such cases the prill must be “parted.”

The filtrate from the gold is then treated with excess of hydrochloric acid and 20 grms. or more of acetate of lead, and a little sulphuric acid added, and the precipitate dealt with as with Claudet liquors (see p. 132).

Assay of Ingot Copper (*Trans. A.I.M.E.*, March, 1895).—The precious metals are determined by assaying 10 samples of 2.5 grms. each, or $\frac{1}{10}$ of an assay ton, by scorification. For the determination of the gold the resulting prills are combined and parted. Often, however, two samples of 25 grms. each are dissolved in 150 c.c. dilute nitric acid (2 parts water, 1 acid), and when the action ceases another 50 c.c. strong nitric are added, and heated till solution is complete. The excess of acid is evaporated off, the solution diluted to about 500 c.c., 3 c.c. of sulphuric acid and 10 c.c. of a saturated solution of acetate of lead added. After stirring well, the precipitate is allowed to settle. The precipitate is filtered, washed, and the beakers cleaned with filter-paper on the end of the finger or a thick glass rod. This is added to the filters containing the precipitate. After drying, the papers are wrapped in thin lead foil and dropped into scorifiers containing about 40 grms. of test lead. Half a gram of borax is added, and the scorification and subsequent cupellation are conducted as usual. It is well, however, to keep the temperature specially low at the commencement of the scorification. For silver, the method is modified by adding, before the lead acetate, a few c.c. of weak salt solution (sufficient to precipitate the silver), and afterwards the sulphuric acid and lead acetate. The scorification and cupellation follow in due course.

Gold and Silver Residues from Electro Refining.—Russell precipitate and silver sulphide may be treated like copper mattes, less quantities (2.5 grms.) being taken, and in scorifying, 8–10 grms. of litharge are added in addition to 20 grms. of test lead.

The ordinary dry assay may also be used. Ten scorifications of 1.25 gm. sulphides, 40 grms. granulated lead, and $\frac{1}{2}$ gm. borax are made, and the buttons cupelled. During scorification the temperature must be low at first, and during cupellation must be very carefully regulated, great care being taken that spitting is prevented. The prills obtained are parted and the gold weighed.

Sweep Assay.—In dealing with sweeps, it is very difficult to sample satisfactorily, owing to the presence of metallic particles in the material. The assay may also be complicated by the possible presence of platinum, aluminium, and other foreign metals.

From 50 to 150 grms. of the sweep is weighed out, and ignited at a low heat on a large scorifier, or on an iron shovel or dish, in a muffle, to remove organic matter. The residue is then well pounded in an iron mortar and sifted through an 80 sieve. The siftings are assayed by crucible method (see p. 139). The flattened scales, if only few, may be assayed by scorification and cupellation. If, however, there are many, they must be melted with 50–100 grms. of test lead in a carbon crucible, thus: The crucible is heated to redness, and the lead introduced. The “scales,” wrapped in thin assay lead, are added, and the mass stirred with a charcoal stick, subsequently poured and carefully weighed. From the button portions or sawings are taken for assay, the weight selected representing some aliquot part of 25 grms., or of the assay ton of sweep by preference.

Inquartation and parting are proceeded with in the usual way. In running down the “sweep” siftings when making a crucible assay, the proportion of borax is increased to remove the oxides of copper, aluminium, etc., which may be present; the charges vary with the character of the sweep, but may be mixed on the following lines:—

1	part (burnt) sweep.	
1	„	sodium carbonate.
1	„	borax.
2	„	litharge.
2–5 grms. argol.		

The button of lead obtained should not weigh less than the weight of burnt sweep taken. Hard buttons are treated by scorification with more lead. See Silver.

MERCURY.

SUBSTANCES in which the metal has ordinarily to be determined.

I. Ores.

II. Amalgams.

Ores of Mercury.—Few minerals containing mercury come under the notice of the assayer.

Native Mercury.—The metal occurs in small globules disseminated through the rock and almost always associated with cinnabar.

Cinnabar is a red mineral varying from a cochineal to dark red in colour. It crystallizes in rhombohedra, but is generally earthy or massive; hardness = 2–2.5; sp. gr. = 8–8.2. Crystals are translucent, and the lustre adamantine. The streak is scarlet. In the open tube sulphur dioxide is given off, and a mirror of mercury formed. In the closed tube it partially sublimes.

More rarely occurring minerals are calomel (mercurous chloride), iodide of mercury, and selenide of mercury. A double sulphide of mercury with bismuth sulphide and zinc sulphide occurs to a limited extent.

CHEMICAL REACTIONS OF MERCURY.

Mercury forms two classes of salts, the mercurous and the mercuric, corresponding with the copper salts, *e.g.* mercurous chloride, Hg_2Cl_2 ; mercuric chloride, HgCl_2 .

The metal is insoluble in hydrochloric acid and in cold dilute nitric and sulphuric acids. It dissolves, on heating, in the two last, forming mercurous or mercuric compounds according to the relative proportions of metal and acid. The metal is readily attacked by free chlorine or bromine.

Wet Reactions.—Mercurous Compounds.—Solutions containing mercury in the mercurous condition give the following reactions:—

1. Hydrochloric acid produces a white precipitate of Hg_2Cl_2 insoluble in nitric acid (after washing). The precipitate is blackened on

adding ammonia, $\text{NH}_2\text{Hg}_2\text{Cl}$ being formed. It is soluble in aqua regia, yielding HgCl_2 .

2. Sulphuretted hydrogen throws down a black precipitate of sulphide soluble in aqua regia.

3. Ammonia gives a black precipitate of a basic salt.

4. Caustic soda and sodium carbonate yield blackish precipitates of Hg_2O and Hg_2CO_3 respectively.

5. Potassium chromate precipitates a red basic chromate, Hg_2CrO_4 , Hg_2O , which brightens on the addition of nitric acid.

6. Acid stannous chloride precipitates white Hg_2Cl_2 , which is immediately reduced on warming, a grey precipitate of metallic mercury resulting.

7. Metallic mercury is precipitated on copper, and other metals introduced into the solution.

NOTE.—Soluble mercurous compounds are apt to deposit basic salts on addition of water. It is, therefore, necessary to keep the solutions distinctly but not too strongly acid.

Mercuric Compounds.—Solutions containing mercury in the mercuric condition behave as follows :—

1. Hydrochloric acid gives no precipitate.

2. Sulphuretted hydrogen produces a precipitate, first white, then red, and, finally, black. The precipitate is insoluble in ammonium sulphide, caustic soda, and dilute acids, but dissolves in boiling aqua regia. The precipitate is also insoluble in potassium and sodium sulphides.

3. Ammonia gives a white precipitate of NH_2HgCl .

4. Caustic soda throws down a yellow precipitate of HgO . If ammonium chloride be present, a white precipitate is thrown down, similar in composition to NH_2HgCl .

5. Sodium carbonate gives a reddish brown precipitate of basic carbonate.

6. Stannous chloride gives first a white precipitate of Hg_2Cl_2 . On further addition and heating the precipitate turns grey, metallic mercury being precipitated. Other reducing agents give similar results.

7. Metallic mercury is precipitated from mercuric salts by copper and other metals.

Dry Reactions.—All compounds of mercury volatilize on heating, either with or without decomposition.

1. Mercuric chloride, mercurous chloride, mercury bromides and iodides, and the sulphide volatilize without decomposition, the chloride yielding a white, the iodide a yellow to red, and the sulphide a red to

black sublimate. The oxidized compounds decompose and yield a film or mirror of mercury.

2. Compounds of mercury, when mixed with anhydrous sodium carbonate and heated in a closed tube, yield a mirror of mercury.

3. The sulphide and selenide yield mirrors when heated in an open tube, the former giving an odour of SO_2 and the latter of horse radish.

The mercurial mirror can be distinguished from the arsenical mirror by cutting off the portion of the tube containing it, and placing it in the lower part of a wider open tube (Fig. 81). Arsenic oxidizes, gives a garlic-like odour, white arsenic being deposited as a sublimate on the side of the tube in microscopic crystals. On washing out the tube with water, adding a drop of dilute caustic soda to the solution and afterwards a drop of copper sulphate, a green precipitate, Scheele's green, is thrown down. If the mirror is mercurial it volatilizes, and is re-deposited higher up the tube, and may be rubbed together into a globule.

The arsenical mirror is blacker, but becomes bright on heating to 200°C. , and may then be readily mistaken for mercury unless tested.

DRY ASSAY.

The estimation of mercury is made by volatilization with or without the condensation of the mercury. The latter yields only approximate results.

Assay of Cinnabar.—By distillation with quicklime and condensation of the mercury. This assay is effected by heating the cinnabar mixed with lime in a glass tube by means of a combustion furnace or its equivalent, *e.g.* a few good Bunsen burners.

A tube, 18 inches long, $\frac{1}{2}$ inch in diameter, is closed at one end, and filled as follows: (a) 1 to $1\frac{1}{2}$ inch of magnesite, MgCO_3 ; * (b) 2 to $2\frac{1}{2}$ inches of quicklime, CaO † (from which the finest dust has been removed); (c) 5 to 10 grms. of the ore mixed with half its weight of quicklime; (d) about 3 inches of quicklime (free from fine powder), and then a loose plug of asbestos. The materials must not be tightly packed, but leave a clear passage for the vapour. This may be ensured by gently tapping the under side of the tube, when a channel will be formed over the top of the assay. The need for a clear passage for the gas must not be forgotten in inserting the asbestos plug.

Another method of securing a clear passage is to insert a thick wire in the tube while filling, and to withdraw it after putting the asbestos

* This is more satisfactory than bicarbonate of soda, which is sometimes used.

† Not hydrate.

in place. The tube is then carefully drawn out over the foot blowpipe into the form shown in Fig. 71. The method of drawing out the tube is to commence heating about 2 inches from the mixture, and when the glass is soft carefully drawing out a little, and by keeping the side near the assay hot, gradually working back towards it till the neck is long enough. The tube is then cut at A.

The tube should be placed in the furnace so that it can be

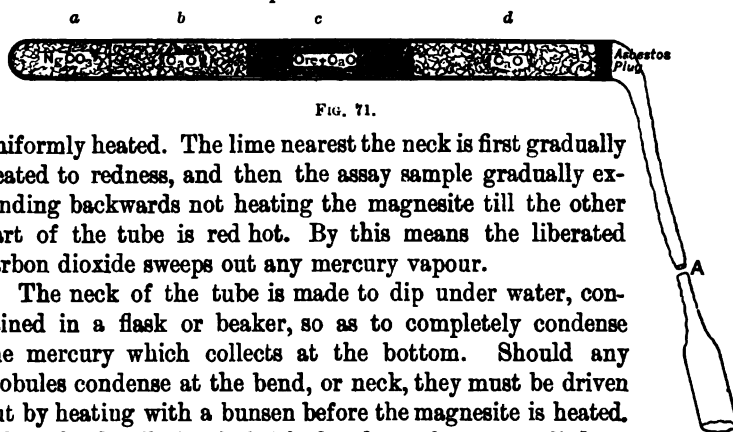


FIG. 71.

uniformly heated. The lime nearest the neck is first gradually heated to redness, and then the assay sample gradually extending backwards not heating the magnesite till the other part of the tube is red hot. By this means the liberated carbon dioxide sweeps out any mercury vapour.

The neck of the tube is made to dip under water, contained in a flask or beaker, so as to completely condense the mercury which collects at the bottom. Should any globules condense at the bend, or neck, they must be driven out by heating with a bunsen before the magnesite is heated. When the distillation is finished, a drop of water applied to the hot neck will break it off, so that any adherent mercury may be removed by washing and rubbing with a bit of filter-paper.

The water is then carefully decanted, and the mercury, with the last drops of water, poured into a roasting-dish, which speedily absorbs the moisture and dries the mercury. If a roasting-dish is not at hand, the mercury may be poured into a porcelain crucible, dried with filter-paper, and gently warmed. The mercury is then weighed.

This method of assay serves for all classes of ore, but the results obtained from iodides are unsatisfactory. These compounds escape decomposition, volatilize, and are condensed with the mercury. In this case the lime should be mixed with iron filings, or a layer of the filings may be placed in the tube next the assay.

In dealing with ores containing mercury as chloride, some difficulty is encountered, owing to the volatile nature of the chlorides. In such cases it is best to mix the lime used with charcoal and a little anhydrous carbonate of soda.

Native Mercury.—Ores containing the whole of the mercury in the native state require no addition, but it is better to deal with them in the same way as cinnabar.

Iron and copper filings, or a mixture of equal parts of lime and

charcoal may be employed. The ores are mixed with from 50 to 60 per cent. of their weight of the mixture.

To avoid breaking the tube, some assayers use an open tube, through which a stream of hydrogen or carbon dioxide is kept passing; but the difficulty of cleaning the neck without breaking it off renders this a doubtful method of saving time. The gas should first be passed through a tube containing copper turnings heated to redness.

Assay of Mercury Ores in a Crucible (Eschka's Process).—In this method of procedure the mercury is condensed on a weighed piece of gold which is used as a cover for the crucible. The method is chiefly used for poor cinnabar and Fahlerz.

The quantity of ore taken varies with the richness.

For ores containing	1 per cent.,	10 grms.
"	"	1-10 "
"	"	-30 "
"	"	over 30 "
"	"	5 "
"	"	2 "
"	"	1 "

The finely powdered ore is weighed in a porcelain crucible, the edge of which has been ground flat, and mixed with half its weight of fine iron filings by means of a glass rod with a rounded end. A layer of iron filings is spread over the assay, and a weighed concave plate of fine gold weighing about 10 grms. is placed over the top of the crucible. The hollow in the plate is filled with cold water, and the crucible (supported on a triangle) is carefully heated by means of a Bunsen burner for about 10 minutes. The reduced and volatilized mercury is condensed on the gold. This is washed carefully with water and afterwards with alcohol, dried by gentle heat (in a water oven), and weighed on a watch-glass. The increase in weight is the amount of mercury in the sample.

In using this method the amount of gold surface presented should be so large that the mercury does not form drops, but condenses as a mirror on the gold plate, which should hold enough water to keep it cool. The iron filings must be free from grease, as this prevents the formation of the mirror, and the cover should fit closely to avoid loss of mercury. The washing with alcohol removes any tarry matters condensed in dealing with bituminous ores.

The gold plate is, after weighing, gently heated in a Bunsen flame to volatilize the mercury, and afterwards reweighed as a check. If the surface becomes spongy it is rubbed gently with the pestle of an agate mortar and heated before again using it.

Assay of Mercury Ores by Loss on Calcining.—Ores containing only native mercury or cinnabar (not both), and in which the gangue is fixed, may be assayed by calcining a weighed portion and estimating the loss.

From 10 to 50 grms. of the ore is taken and heated to dull redness in a crucible, with occasional stirring. After the mercury has been expelled, or, in the case of cinnabar, the sulphur has burnt off, about 5 to 10 grms. of ammonium carbonate is added and carefully heated till the salt is completely volatilized. The residue is weighed, 232 parts loss in the case of cinnabar is equivalent to 200 of mercury.

This method is inaccurate, and in most cases inapplicable, *e.g.* in the presence of other sulphides, bituminous matter, and substances that lose water, or decomposable carbonates.

Mercury ores may also be assayed in iron or earthenware retorts, when the quantity of material operated may exceed 20 grms., with a cooled flask as a receiver. The neck of the retort must be carefully cleaned.

Arsenical Ores.—According to Berthier, the best method of treating arsenical ores, is to heat them with from 4 to 5 times their weight of litharge, with which the arsenic compounds form a slag, while the cinnabar is decomposed, metallic mercury and sulphur dioxide passing over. The former is condensed in the usual way.

Mercury in amalgams may be estimated by placing the sample in a tube through which a current of hydrogen or carbon dioxide is passed while heat is applied, and weighing the condensed mercury. For sodium amalgams a weighed quantity is treated with water, and the residual mercury washed, dried, and weighed.

WET PROCESSES.

Wet methods of assaying mercury are not generally employed.

The substances usually associated with cinnabar are limestone, oxide of iron, bituminous matter, clay, and occasionally metallic sulphides, etc.

The weighed sample is first digested with hydrochloric acid for some time, allowed to settle, and the solution decanted. The residue is treated with aqua regia, which dissolves the mercury as chloride. The solution is decanted, the residue washed, and the liquid evaporated to small bulk. Sulphite of soda is then added, which reduces the iron to the ferrous condition, the liquid boiled to expel sulphur dioxide and saturated with sulphuretted hydrogen which throws down the mercury as sulphide, HgS .

The precipitate is filtered on a tared paper and washed thoroughly, first with water, then with alcohol, and finally with carbon disulphide to remove separated sulphur, dried at 100°C ., and weighed. If arsenic or antimony be present the precipitate must be digested with yellow ammonium sulphide, and thoroughly washed before weighing. If the presence of other metals is suspected, the precipitate, after washing

till free from hydrochloric acid, is digested with dilute nitric acid for some time. Any free sulphur that separates may be completely removed by digesting—after thorough washing—with alkaline sodium sulphite, and any lead sulphate by means of sodium acetate. The residue is filtered, washed, dried at 100°C ., and weighed. Factor for Hg = 0.86202.

Electrolytic Assay.—This method of procedure is suitable for ores in which foreign metallic matters give rise to complication, owing to the impurity of the precipitate obtained by sulphuretted hydrogen.

From 1 to 5 grms. of the ore is digested for some time with hydrochloric acid in a conical flask to remove soluble matters (antimony and bismuth sulphides, carbonate of lime, hydrated ferric oxide, etc., are dissolved). The clear liquid is carefully decanted, the residue boiled with hydrochloric acid, and potassium chlorate added in small portions at a time. When solution is complete, the liquid is boiled, to expel chlorine, filtered, and the residue washed.

The iron salts are reduced by sodium sulphite or sulphurous acid, and the hot liquid saturated with sulphuretted hydrogen. After filtering and washing, the precipitate is digested with ammonium sulphide, to remove any arsenic and antimony, and carefully washed.

The residue is treated with nitric acid, sp. gr. 1.12, to remove soluble sulphides, and filtered. The precipitate is dissolved in aqua regia. Any sulphur that separates, if clean, may be neglected. The liquid is evaporated to small bulk, diluted to about 50 cc., transferred to a weighed platinum dish, and a few drops of sulphuric acid added. The dish is placed on a brass plate, connected with the negative pole (zinc) of a Bunsen battery of four cells. A small strip of platinum foil connected with the carbon pole forms the positive electrode. This is supported in the liquid horizontally. On passing the current some mercury is first deposited as subchloride, but this is afterwards gradually reduced, and mercury remains. The precipitation takes about an hour to an hour and a half. The liquid is decanted or withdrawn by a pipette, and the mercury washed with water, alcohol, and ether successively, and gently warmed to dry it. The dish and its contents are weighed. The increase in weight is the mercury deposited. The separation of the mercury from compounds of copper, arsenic, tin, antimony, and bismuth in the preparation of the solution is very important, as on it the accuracy of the assay principally depends.

Estimation of Mercury as Mercurous Chloride (Rose's Method).—The most satisfactory method of precipitating the chloride is by the addition of phosphorous acid. In preparing the solution the mercury must be converted into mercuric chloride, and filtered as above. The iron salts are reduced by sulphurous acid or sodium sulphite, and

hydrochloric acid added. Phosphorous acid is then added, and the liquid allowed to stand for 12 hours. The precipitated chloride, Hg_2Cl_2 , is collected on a weighed filter paper washed by decantation and on the filter with warm water, and dried at 100°C . Factor for Hg = 0.8496.

Other reducing agents, *e.g.* formates, stannous chloride, etc., yield very indifferent results, owing to the complete or partial reduction of the mercurous chloride to metallic mercury. Phosphorous acid does not effect this reduction, especially in the presence of hydrochloric acid, unless heated beyond 60°C . Nitric acid and all oxidizing agents should be absent, but a little of the former does not interfere, if the solution be sufficiently dilute.

Detection of Mercury in Ores (Smithson modified).—A particle of ore is treated with aqua regia in a porcelain capsule, and the nitric acid removed by boiling. The remaining liquid is diluted, and a drop placed on a gold coin or gold leaf, and a fragment of tin placed in it resting on the gold. If mercury be present, even in traces, a white stain will be produced. It is just possible the stain may be tin that has dissolved; but on warming the coin, if it be mercury, it will volatilize. This test is not satisfactory in the presence of arsenic, which is also deposited as a more or less bright mirror.

IRON.

THE materials in which the determination of iron is required are—

Class I.—Oxidized ores, carbonates, and slags.

Class II.—Sulphurized ore and mattes.

Class III.—Metals. Iron and steel, etc.

Iron Ores.—*Class I.*—**Magnetite**, Fe_3O_4 , is an iron-black, heavy mineral, sp. gr. 5, hardness 5·5–6·5. Crystals, regular octahedra. Streak—black. Magnetic, and often polar. Soluble in hydrochloric acid, yielding a mixture of ferrous and ferric chlorides, and gives iron reactions with borax.

Ilmenite or **Menacannite** has a metallic lustre, and a leaden grey or iron-black colour; is often crystalline; hardness 5–6, sp. gr. 4·6. It consists of a double oxide of iron and titanium.

Titaniferous Iron Sand is a black sand with a high lustre, consisting mainly of a mixture of ilmenite and magnetite.

Franklinite.—An iron-black mineral, with a dark brownish-red streak. It consists of ferric and manganic oxides, with ferrous and zinc oxides, $(\text{FeZn})\text{O}(\text{MnFe})_2\text{O}_3$. It is usually slightly magnetic, and is generally associated, and often intimately mixed, with red zinc ore.

Red Hematite, Fe_2O_3 , occurs as kidney iron ore, and in massive and earthy forms (red ochre). It has a sp. gr. varying from 4·2–5·1; gives a fine red streak. The hardness is variable.

Specular Iron Ore is the crystallized variety of red hematite, and occurs usually in conjunction with hematite; the crystals are modified rhombohedra, or flat plates; the colour is black, and the lustre metallic and splendent, sometimes iridescent. Micaceous iron ore is a foliated variety composed of thin scales. Specular ore gives a reddish streak.

Brown Hematite, **Göthite**, **Limonite**, **Bog Iron Ore**, **Yellow Ochre**.—These all consist of ferric oxide, combined with varying amounts of water; they vary greatly in hardness, density, and general character, and all give a yellow or brown streak.

Turgite is a hydrated oxide, containing very little water; it is reddish black or purplish in colour, and the streak is a dark reddish brown.

Göthite crystallizes in radiating groups of crystals, and has a semi-metallic iron-black or brownish-black colour; limonite or brown hematite

is dense and compact, and generally dark brown in colour. Bog ores are less compact, brown or yellowish-brown, and sometimes earthy.

All these hydrates are included under the term, Brown Iron Ores.

Siderite, Chalybite, Spathic Iron Ore, Carbonate of Iron, FeCO_3 , is a sparry crystalline mineral of varying colour, from yellowish white to reddish brown; it gives a white streak; its hardness is 4, and its sp. gr. 3-4. Before the blowpipe it yields a black mass or globule, which is magnetic; it dissolves in acids, but only effervesces freely in hot hydrochloric acid.

Clay Iron-stone is a compact mineral, which emits a clayey odour when breathed on; it is a mixture of carbonate of iron with more or less clay, etc.; its hardness is between 3 and 4; it is partly soluble in hydrochloric acid.

Blackband Iron-stone is clay iron-stone intimately mixed with coaly matter; it is generally brownish-black, compact. It often has a banded appearance.

Class II.—Iron Pyrites. See SULPHUR.

Mispickel. See ARSENIC.

Products.—Class I.—Burnt Ore, Blue Billy.—The residue of ferric oxide left when pyrites is burnt for the removal of sulphur.

Purple Ore.—The residue of finely divided ferric oxide left after the treatment of burnt pyrites for the extraction of copper by wet processes.

Calcined Iron-stone.—The residue left on calcining clay and blackband iron ores.

Tap Cinder, Best Tap, and other slags consisting mainly of ferrous silicate are black or bluish-black slags, with a dull or metallic lustre.

Class II.—Copper Mattes, and other reguli, varying from brittle, bronzy, granular bodies, to compact, white, semi-metallic substances, are mixtures of copper, iron, and other sulphides.

Nickel Speiss, hard, yellowish-white, semi-metallic and brittle, is a mixture of arsenides.

Class III.—Meteoric Iron.

Pig Iron.—Iron containing variable quantities of carbon silicon, and other elements; may vary from being largely crystalline and dark grey (grey iron) to very fine-grained and almost silver white and crystalline (white iron). The grey varieties are comparatively soft; the white irons are very hard and brittle.

Spiegeleisen is largely crystalline, hard, brittle, with brilliant metallic lustre; it contains up to 25 per cent. manganese.

Ferromanganese is granular, hard, faintly yellowish; it contains up to 85 per cent. manganese.

Siliconeisen and Silicoferro-Manganese.—Contain up to 16 per cent. of silicon. They often resemble grey pig iron in structure, but have a whiter lustre.

Refined and Washed Iron.—Pig iron from which the bulk of the silicon has been removed, but containing up to 3.5 per cent. carbon under 0.2 per cent. silicon.

Wrought Iron.—The fibrous product obtained by rolling puddled iron. It is tough, malleable, and ductile.

Ingot Iron and Mild Steel.—The softer metals obtained by the Bessemer and Open Hearth processes, containing up to 0.5 per cent. carbon, with small quantities of manganese, and traces of sulphur, phosphorus, and silicon.

Steel.—The varieties of iron containing a larger proportion of carbon than mild steel, but less than pig iron.

CHEMICAL REACTIONS OF IRON.

Dry Reactions.—Mixed with fusion mixture, and heated on charcoal before the blowpipe, in the reducing flame, iron compounds yield a black magnetic mass. Those containing sulphur must first be roasted in the oxidizing flame.

Heated in borax on platinum wire a yellow bead is obtained in the oxidizing flame, which becomes colourless on cooling, if the quantity of iron be small. A bottle-green bead is obtained in the reducing flame.

Wet Reactions.—Two of the iron oxides yield salts.

Ferrous salts from ferrous oxide, FeO ; *e.g.* FeCl_2 , FeSO_4 .

Ferric salts from ferric oxide, Fe_2O_3 ; *e.g.* Fe_2Cl_6 , $\text{Fe}_2(\text{SO}_4)_3$.

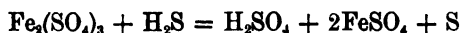
By oxidation ferrous are converted into ferric salts, and by reduction, ferric into ferrous salts.

Ferrous Salts.—Solutions containing iron in the ferrous state behave as follows :—

1. Hydrochloric acid and sulphuretted hydrogen give no precipitate.
2. Ammonia, or caustic soda, gives a whitish precipitate of ferrous hydrate, which rapidly darkens, and on prolonged exposure, or shaking, becomes red brown, being converted into ferric hydrate.
3. Sodium carbonate gives a white precipitate, which darkens on exposure.
4. Potassium ferrocyanide gives a light bluish precipitate.
5. Potassium ferricyanide gives a dark blue precipitate.
6. Potassium sulphocyanate gives no coloration.

Ferric Salts.—Solutions containing iron in the ferric state give the following reactions :—

1. Hydrochloric acid and sulphuretted hydrogen give a white precipitate of sulphur. The ferric salt is reduced to the ferrous condition—



2. Ammonia or caustic soda gives a red-brown precipitate of ferric hydrate ($\text{Fe}_2\text{H}_6\text{O}_6$), readily soluble in acids.

3. Sodium acetate in neutral solutions gives on boiling a red-brown precipitate of basic ferric acetate.

4. Potassium ferrocyanide gives a precipitate of Prussian blue, which is decomposed by caustic soda.

5. Potassium ferricyanide gives a greenish brown, or brown coloration.

6. Potassium, or ammonium sulphocyanate, gives a deep blood-red coloration.

7. *Experiments.*—Heat a solution of a ferric salt to boiling, to one portion add a little zinc, and when quite colourless add a little potassium sulphocyanate. No coloration results, showing the complete reduction to the ferrous state. Add a drop of potassium bichromate solution, and note the instant production of the blood-red colour.

8. To another part of the boiling solution add sodium sulphite, or sodium thiosulphate (Hypo), and test as before. The sulphite reduces the iron to the ferrous state.

9. To another portion add stannous chloride, and test as before. A similar reduction occurs.

10. Add nitric acid or other oxidizing agent to a solution of a ferrous salt; note the darkening in colour—the iron is oxidized to the ferric condition. Test the solution as before.

DRY ASSAY OF IRON.

The use of dry methods for the assay of iron ores is almost obsolete, owing to the uncertain character of the results. As the product is cast iron, and consequently contains carbon and silicon, the result is always higher than the real iron contents. It, however, gives approximately the quantity and quality of iron which would be obtained in the furnace.

Method of conducting the Assay.—The assay is conducted in carbon-lined (brasqued) crucibles. By this means the addition of charcoal to the assay mixture is obviated, and interference with the fusibility of the slags prevented. Either the small crucibles prepared in

the laboratory or special pots (iron assay crucibles) are employed, although the ordinary Cornish crucible will withstand the heat. The special form is tall and narrow, and permits of several crucibles being placed together in a small space.

In assaying an unknown ore, four trials are generally made, of different mixtures of fluxes, in order to find that which gives the best and most fluid slag. For silicious ores the fluxes are basic, and *vice versa*. The crucibles are marked under the bottom or under the lid, with red hematite, and fixed by clay lute on a piece of firebrick. The whole (after drying) is placed in the furnace, resting on the fire bars, and the fire made round it. After the necessary heating the crucibles are removed, broken, and the buttons examined. That giving the best results, as indicated by the slag, is taken as correct, or the assay is repeated with such slight variation as may be indicated by the result.

The crucibles are prepared as follows :—Black treacle (molasses) is mixed with its own volume of water and kneaded into charcoal powder, or lampblack, to form a stiff paste, which breaks short. This is rammed into the crucible till it is full, and a cavity cut out with a knife or cutter, and afterwards shaped with a smooth stick or a plug (Fig. 72). The crucibles are carefully dried and heated in a close muffle, mouth downwards, embedded in charcoal powder. When heated the sugar decomposes, and the carbon left cements the charcoal powder so as to form a firm lining. If no muffle is at hand, the pots may be filled with dry charcoal powder, closely covered, and gradually heated up in a wind furnace. This lining not only prevents the charge from coming into contact with the silica of the pot, but serves as a reducing agent for oxides, and at the same time gives support to the walls of the crucible, which might soften at the temperature employed.

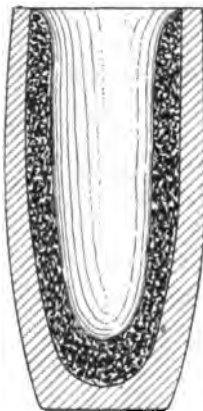


FIG. 72.

Assay of an Ore of Unknown Composition.—Prepare four test mixtures thus :—

		No. 1.	No. 2.	No. 3.	No. 4.
Ore	...	10·0	10	10	10 grms.
Lime	...	2·5	2	2	4 „
Silica	...	2·5	3	4	1 „

An addition, from 2·5 to 10 grms., of fluor spar is made when the ore contains titanium.

Or—

Ore	...	10.0	10.0	10	10.0 grms.
China clay		2.0	2.0	2	2.5 „
Lime	...	2.5	2.5	1	4.0 „
Sand	...	2.5	1.0	2	— „

Or—

Ore	...	10.0	10.0	10.0	10 grms.
Lime	...	3.0	2.5	1.5	4 „
Glass	...	2.5	2.5	4.0	1 „

No. 1 is suitable for pure ores containing little gangue, *e.g.* red hematites, etc.

No. 2 for ores containing clay and silica, *e.g.* clay iron-stone.

No. 3 for spathic iron ores and calcareous hematites, and others containing lime, magnesia, and manganous oxides in quantity.

No. 4 for very silicious ores.

The crucibles are filled and the charge covered with a plug of charcoal. The lid is marked with red hematite underneath, and luted on.

NOTE.—A good fire lute consists of 1 part fire clay, 3 parts sand, and a little hair or horse-dung moistened with borax water. Ganister, mixed with hair, does well. Or, 1 part China clay, with 6 to 7 parts of fine sand, with a little hair and borax water. Dry zinc oxide, mixed with powdered borax, and wetted to a satisfactory consistency, is also a good fire lute.

The four crucibles are placed upright on a piece of brick, and luted on, their positions being noted. The whole is carefully and completely dried.

While drying, the furnace is cleaned and made ready. When dry the brick is placed on the fire bars, and the fire made round it. Hard coke or anthracite is used for firing, and the temperature gradually raised to whiteness, at which it is maintained for 1 to 1½ hour or longer, and the fire is then allowed to burn down. The crucibles are removed, and, after cooling, carefully broken. The buttons of iron, with the adherent slag, are turned out into the hand and put aside on numbered places. The contents of each crucible are weighed; the loss is due to the oxygen, etc., removed from the ore, and serves as a check on the result. Afterwards the iron button is detached, the slag crushed, and any shots of iron extracted by a magnet. These, with the main button, are weighed.

Indications of Slags.—The slags should be well fused, and adhere but slightly to the button. The latter should be well formed, with a rounded edge.

Dark, semifused, or resinous slags with a greenish tint indicate excess of silica. Stony, rough, or even highly crystalline dull slags usually

indicate excess of bases, while if the product is only fritted, and the reduced iron has not collected, there is probably a deficiency of both alumina and silica. Probably magnesia and lime are present in excess.

The impurities in the ore may be judged from the colour of the slag. Manganese, amethystine to green, yellow green, or brown.

Titanium gives a black slag, more or less resinous or scoriaceous, and curiously wrinkled. Sometimes the blue colour of slags is attributed to this element.

Chromium gives a dark slag, sometimes with a metallic iridescence.

Normal slags are greyish, well fused, and neither very glassy nor stony in character.

Indications of the Button.—The buttons are placed in a bit of thin sheet tin, and tested with a hammer on the anvil. Good buttons should be well formed, should flatten slightly before breaking, and exhibit a grey or greyish granular fracture.

Phosphorus renders the metal hard, brittle, and somewhat whiter.

Sulphur makes the button strong, hard, and white, and causes it to break without flattening.

Manganese renders the button hard, white, and highly crystalline, and probably non-graphitic.

Titanium is said to render the button smooth, grey, and cause it to adhere to the slag.

Chromium.—The button is very smooth, very white (almost tin white), crystalline, hard, and brittle. If the chromium is very high the fusion may not be complete, and a spongy half-fused mass, varying in colour from white to a clear grey, may result.

Nickel produces no appreciable effect; the button is tough and strong.

If one of the mixtures gives good results, the assay is repeated with it. Results should not vary more than 0.5 per cent.

Assay of Ores of known Composition.—In this case the slag is made to conform to some well-known formula. Percy's slag,* which has the formula $3(2\text{RO}, \text{SiO}_2)2\text{R}_2\text{O}_3, 3\text{SiO}_2$, is a mixed monosilicate in which RO stands for any monoxide base, such as CaO, MgO, and R_2O_3 for any sesquioxide, such as Al_2O_3 .

It contains—

RO	47 per cent., <i>i.e.</i> roughly 3 parts.
R_2O_3	15 " " 1 "
SiO_2	38 " " 2½ "

The sesquioxide base is employed as China clay, $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$, containing after dehydration nearly equal quantities of SiO_2 and Al_2O_3 ;

* See Percy, vol. i. p. 23, for analysis.

consequently, as one of Al_2O_3 in the slag is proportionally equal to $2\frac{1}{2}$ of SiO_2 , three-fifths (*i.e.* $1 - \frac{1}{2\frac{1}{2}}$) of the Al_2O_3 in the China clay is available as a flux. The silica thus added must be added to that already present before determining the lime to be added.

Examples.—An ore contains—

No. 1.	per cent.	10 grms. contain	slag should contain	to be added
SiO_2	2.5	0.25	2.5	2.25
Al_2O_3	10.0	1.00	1.0	—
CaO	5.0	0.50	3.0	2.5

These additions are all that are necessary.

No. 2.	per cent.	10 grms. contain	slag should contain	to be added
SiO_2	15.0	1.5	2.5	1.0
Al_2O_3	—	—	1.0	1.0
CaO	0.5	0.05	3.0	2.95

Here both silica and Al_2O_3 are required, and as the amounts are equal, two parts (grms.) of China clay will supply both.

No. 3.	per cent.	10 grms. contain	slag should contain	to be added
SiO_2	25	2.5	2.5	—
Al_2O_3	—	—	1.0	1.0
CaO	—	—	3.0	3.0

If two parts of China clay be added to furnish the alumina one part of silica will also be added, and this is not required.

Proceed thus. As shown above, the fluxing power of the China clay is $\frac{2}{3}$ of the Al_2O_3 . Since it contains only half its weight of Al_2O_3 , its fluxing power for silica is $\frac{\frac{2}{3}}{2} = \frac{3}{10} = 0.3$ of its weight.

Now, to produce a slag of the above constitution, one part of Al_2O_3 is required. $\frac{1}{0.3} = 3.333$, but that adds $\frac{3.333}{2}$ of silica = 1.666 parts.

\therefore total $\text{SiO}_2 = 2.5 + 1.666 = 4.166$,

and lime required to maintain constitution =

$$\frac{4.166}{2.5} \times 3 = \frac{12.5}{2.5} = 5$$

The charge is made to contain 10 grms. ore, 3.333 China clay, and 5 grms. lime; and slag contains

SiO_2 4.1666 grms.
 Al_2O_3 1.666 "
 CaO 5.0 "
 and $\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{CaO} :: 2.5 : 1 : 3$

If an assay be unsatisfactory, the slags must be examined, and an opinion formed as to the cause. Trial assays are then repeated till good results are obtained.

WET METHODS OF ESTIMATION.

Solution.—Oxidized ores of iron should be reduced to the finest possible state of division, and treated with strong boiling hydrochloric acid, without any addition of nitric acid or other oxidizing agent, and boiled till solution is complete, or the residue is white. If a method be used in which the presence of tin in solution is not objectionable, a few scraps of that metal greatly facilitates the solution of difficultly decomposable ores.

In the case of titanitic and other difficultly soluble ores, recourse may be had to heating the ore with hydrochloric acid under pressure (as proposed by Mr. A. H. Allen). The easiest method of effecting this is as follows. A portion varying from 0.5 to 1 gram. is weighed out in a little platinum boat made from a bit of platinum foil. A piece of combustion tubing, about 10 inches long, is carefully closed at one end over the blowpipe and nearly half filled with strongest hydrochloric acid, the weighed sample is slipped in and the open end carefully drawn out and sealed. The tube and its contents are heated for about two hours in a water bath, and then in an oil bath, or better in a "cannon" furnace between 140° and 150° C. till decomposition is complete. When cold the end of the tube is broken under water, the contents transferred to a beaker, and the determination proceeded with.

Another method of dealing with very refractory ores is to fuse the weighed sample with bisulphate of potash in a platinum crucible for 25 minutes, boiling out the residue and dissolving in acid. This treatment yields the total iron in a form soluble in hydrochloric acid.

Slags.—Basic iron slags may be decomposed, and the iron obtained in solution by digestion with hydrochloric or sulphuric acids; but if refractory the following method perfected by Welbur and Whittlesey may be employed. The ore is intimately mixed with from its own to double its weight of finely powdered fluor spar free from iron (cryolite will also serve), and digested with hydrochloric acid in a platinum crucible in a water bath till the iron is dissolved. If it is desired to estimate the iron present as protoxide as well as peroxide the crucible must be protected during solution, either by carbonic acid gas or coal gas (see p. 181).

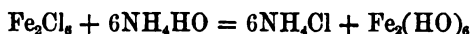
The solution of metallic iron will be dealt with in Part III. The solutions obtained will contain the iron as a ferric or ferrous salt,

according to the method of solution adopted, and the composition of the material.

If dissolved without access of air (see Fig. 74), the iron will be present in the same condition as in the material treated.

GRAVIMETRIC METHODS.

Estimation of Iron as Ferric Oxide.—This is almost the invariable method employed for estimating iron gravimetrically. It gives only total iron. The iron in the solution is peroxidized by boiling with a little strong nitric acid, diluted and excess of ammonia or caustic soda added.



The iron is precipitated in a flocculent form as ferric hydrate, which, on boiling, becomes more granular. This is filtered, washed free from chlorine, dried in an air-bath, ignited, and weighed as Fe_2O_3 . The whole of the iron must be in the ferric state, the solution precipitated as hot as possible, or the precipitate will retain foreign matters, boiled to ensure easy filtration, and washed free from chlorine, or loss will occur on ignition. The ignition temperature should not exceed bright redness.

In the presence of large quantities of fixed salts the precipitate may be freed from them by dissolving in hydrochloric acid, after filtering, and again precipitating with ammonia. This method is inapplicable without previous separation (see Analysis of Iron Ores) in the presence of substances precipitated by ammonia, *e.g.* aluminium, chromium, manganese, tin, and phosphoric and arsenic acids.

Estimation of Iron in Burnt Ore.—Weigh out 0.5 gm. of the dried and finely divided material on a watch glass, transfer to a beaker, cover with 10 c.c. strong hydrochloric acid, and heat on the hot plate till dissolved. Dilute to 50 c.c., filter off any insoluble residue, and wash; if necessary, moisten the paper with hydrochloric acid, to complete the removal of the iron. Heat the solution and cautiously add ammonia (1 part water, 1 part ammonia) till strongly alkaline, and boil for some time. Let settle, decant through a filter, and wash three or four times by decantation, using about 50 c.c. wash water each time. Transfer the precipitate to the filter, wash thoroughly with hot water. Dry the precipitate, burn the filter in a weighed crucible, add the precipitate, ignite, and weigh (p. 52, Factor for Iron) = 0.7.

$$\text{Fe}_2\text{O}_3 = 2 \times 56 + 3 \times 16 = 160 \quad \frac{112}{160} = \frac{7}{10} = 0.7$$

VOLUMETRIC METHODS.

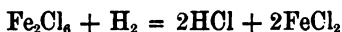
These are based on the facility with which ferrous salts can be converted into ferric salts by oxidizing agents, or ferric salts reduced to the ferrous condition by reducing agents, and the readiness by which the completeness of the change can be ascertained. In estimating total iron, it is necessary that the whole shall exist in one or other form, and in estimating iron in both states the solution must be effected under conditions which do not alter its condition.

The methods of estimation generally employed are—

1. Oxidation to the ferric state by potassium permanganate solution.
2. Oxidation by means of potassium bichromate.
3. Reduction by means of stannous chloride solution.
4. Reduction by means of cuprous chloride solution.

Methods of Reduction.—In carrying out methods of assay which involve the oxidation of the iron, it is necessary to reduce any iron existing in the solution in the ferric state to the ferrous condition prior to titration with the standard solution.

Reduction by Means of Zinc in Acid Solution.—This is effected by adding to the acidified solution pure zinc, granulated, or in the form of a rod. The nascent hydrogen liberated rapidly reduces the iron salt thus :—



The solution should be kept concentrated (not exceeding 50 c.c.) and hot. The reduction is best effected in a flask with a funnel in the mouth, or the mouth may be stopped by a cork fitted with a Bunsen valve. This consists of a short bit of stout rubber tubing, with a slit, cut lengthwise in the tube (Fig. 73), fitting on the end of a short glass tube which just passes through the cork. The other end is stopped with a short piece of glass rod. By this means the gas generated in the flask can escape, but

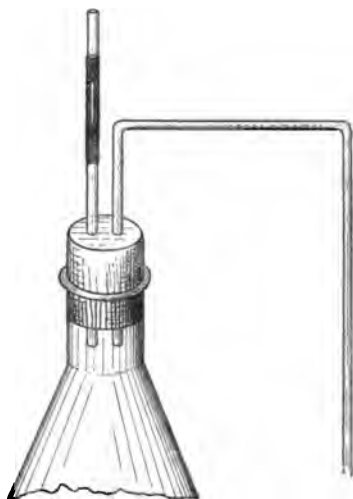


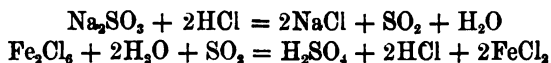
FIG. 73.

no air can enter. When the flask is removed from the hot plate the cork should be eased to enable the air to enter as the enclosed gas contracts, or the flask may collapse under the air pressure, or a side

tube dipping under boiled water may be introduced, as shown, when the water is drawn over as contraction proceeds. The latter is the better method.

The action of the zinc is continued till the colour of the ferric salt is destroyed, or till a drop withdrawn on the point of a glass rod gives no coloration on a spot plate with a drop of potassium sulphocyanate. The solution is then diluted with boiled water, and filtered through glass wool (a plug of which is loosely inserted at the top of the funnel stem), to remove the residual zinc and floating particles, into a beaker or dish for titration. The filter is washed with boiled water.

Reduction with Sulphurous Acid Gas.—For this purpose the warm solution should be saturated with sulphur dioxide, or a solution of the gas may be employed. The excess is removed by boiling. Sulphur dioxide may be generated by heating copper with sulphuric acid, or kept in solution for use. It is, however, procurable in the liquefied form in syphons. Sodium sulphite, or, better, potassium metabisulphite, may be used. In this case the solution must be acid, and the salt added in small quantities at a time in the solid condition; any excess must be decomposed by hydrochloric acid, and the sulphur dioxide removed by boiling.



Sodium bisulphite may also be employed.

Reduction with Sulphuretted Hydrogen.—In this method any nitric acid should first be removed by evaporation with hydrochloric or sulphuric acid, the liquid diluted and saturated while warm with sulphuretted hydrogen. This will precipitate sulphur and also sulphides of silver, mercury, copper, lead, bismuth, tin, arsenic, antimony, and cadmium, if those metals are present. The solution is then boiled till free from H_2S (shown by the vapour not discolouring filter paper moistened with lead acetate solution), during which the sulphur will coagulate, and the liquid is filtered for titration. The reduction is rapid.



Reduction by Ammonia and Ammonium Sulphide.—After adding excess of the reagents, hydrochloric acid is added in excess, the liquid boiled to expel sulphuretted hydrogen, and the solution filtered.

Reduction by Thiosulphate of Soda.—This is effected in very slightly acid solution in the same manner as with sodium sulphite. The solution is boiled till all sulphur dioxide is expelled and the sulphur filtered off, as with sulphuretted hydrogen. Any aluminium in the solution is precipitated.



The sulphur is precipitated by a reaction between the hydrochloric acid and the thiosulphate. The end of the reaction must be determined by potassium sulphocyanate on a spot plate.

Reduction by Stannous Chloride.—The solution is boiled and a solution of stannous chloride added cautiously till the colour is destroyed, and a minute drop gives no colour with potassium sulphocyanate on the spot plate, or the complete reduction of the iron may be indicated by the reagent (platinic and mercuric chloride) given on p. 180. This is the most rapid method of reduction.

Reduction of Iron in Hydrogen before Solution.—The sample of ore is weighed in a small porcelain or platinum boat, and introduced into a porcelain tube heated in a combustion furnace. A current of air or oxygen is first passed over it to remove organic matter and sulphur. This is complete in from 15 to 20 minutes. Hydrogen is then passed through till the ore is reduced to the metallic state. This requires from 1 to 1½ hour, and the tube is allowed to cool with the hydrogen still passing through. The boat is then withdrawn and dropped into a flask fitted with a Bunsen valve containing hot dilute sulphuric acid, into which a little bicarbonate of soda has been introduced to generate CO₂ and displace the air. The iron dissolves, giving a solution of ferrous sulphate. In this method total iron, both in oxide and sulphide, is given. Titaniferous iron ores do not give good results, an insoluble residue always remaining, which contains iron.

Ores containing titanium should be reduced by sulphur dioxide or sodium sulphite when oxidation methods are used in estimating the iron.

Peroxidation of Iron Solutions.—The difficulty is to effect this completely, without leaving an excess of the oxidizing agent, which would vitiate the results.

Oxidation with Potassium Permanganate.—This is the most convenient method when the iron is to be estimated volumetrically. The solution of permanganate is added cautiously drop by drop to the diluted solution (which must not contain more than 0.5 m.g. (0.0005 gm.) per c.c.) till a faint pink tint is produced. All the iron is then in the ferric state.

Potassium bichromate may be used, but it is necessary to test with potassium ferricyanide on a spot plate for the end of the reaction. See p. 177.

Lead peroxide may be employed in neutral or faintly acid solutions, but the solution must be boiling, and requires filtering to remove excess.

Hydrogen peroxide in acid solution gives good results, the excess being removed by prolonged boiling.

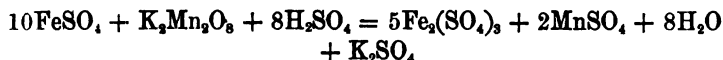
Potassium chlorate added with hydrochloric acid, and evaporation to dryness with excess of acid to decompose the salt and expel chlorine, is an excellent method of oxidation.

Bromine water in acid solution may also be used, the excess being removed by boiling.

POTASSIUM PERMANGANATE METHOD.

For this purpose the iron must be in the ferrous condition, preferably in sulphuric acid solution. This may be obtained by dissolving in sulphuric acid or by evaporating to small bulk with sulphuric acid, thus expelling hydrochloric acid.

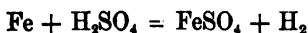
The permanganate solution used for titration oxidizes the ferrous salt to the ferric condition, and owing to the high tinctorial power of the substance the slightest excess is rendered evident by the pink colour.



Standard Solution of Potassium Permanganate.—Weigh 3.165 grms. of the salt, dissolve it in water, and dilute to a litre.

This solution must be restandardized from time to time, as it does not keep well.

Standardizing.—It must be standardized with pure iron. Dissolve 0.5 grm. of pure iron wire (or piano wire = 99.8 per cent. of iron) in 50 c.c. dilute sulphuric acid in a flask fitted with a Bunsen valve. Before dropping in the iron, expel the air by putting a little pure bicarbonate of soda into the flask. Warm till solution is complete. Dilute the solution to 500 c.c. with boiled water.



Measure off 200 c.c. with a pipette into a white porcelain dish or a beaker, and titrate, stopping immediately a pink tint is produced.

Repeat with another portion, and take the mean of the results, thus—

No. 1, volume of solution used	35.65
No. 2, " " "	35.75
			<hr/>
No. of determinations	...	2)	71.4
			<hr/>
			35.7

200 c.c. of the iron solution contain $\frac{200}{500} \times 0.5$ grms. iron = 0.2.

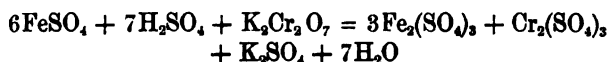
$$\frac{0.2}{35.7} = 0.0056 \text{ gm. iron.}$$

If pure iron is not at hand, pure oxalic acid may be used for standardizing; 90 parts of oxalic acid are equivalent to 56 of iron.

This method is unsuitable for the estimation of iron in ores containing organic matter, as this acts on the permanganate and gives high results, and is only applicable in solutions containing only iron salts.

POTASSIUM BICHROMATE METHOD.

This is the method most commonly used for the estimation of iron. When potassium bichromate is added to an acid solution containing iron in the ferrous state, the following reaction takes place—



The ferrous salt is oxidized, and the colour of the solution changes to green, owing to the chromium salt formed. The end of the reaction is determined by testing small drops of the solution with a freshly prepared solution of potassium ferricyanide on a porcelain tile or spot plate. When the whole of the ferrous salt has been oxidized, the solution ceases to give a blue colour with the ferricyanide. See Reactions for Iron, p. 165.

Standard Solution of Potassium Bichromate.—Weigh 8.762 grms. of the pure salt, dissolve it in water, and make up to a litre. 1 c.c. of this solution = 0.01 gm. iron. A solution of half this strength is also frequently employed.

Solution of Potassium Ferricyanide.—This must be freshly made and very dilute, only a faint yellowish tint should be visible. The spot plate used may be a plain tile, or a colour-testing plate with cavities.

Standardizing.—Although the salt is definite in composition and not liable to decompose, the solution should be standardized. Dissolve two quantities of about 0.5 gm. of pure iron wire, in conical flasks fitted with Bunsen valves, in about 100 c.c. of dilute hydrochloric acid (1 : 1), as described (p. 173). When dissolved, transfer each to a white porcelain dish, and rinse out the flasks thoroughly with boiled water. Make up to about 150 c.c. Run in the bichromate solution slowly, with continual stirring. When about 40 c.c. of the solution has

been added, put some spots of ferricyanide on the tile, and test a small drop of the solution. The blue coloration will be strongly marked. Run in the solution cautiously, and test from time to time. When the blue colour becomes faint test after every few drops, till no colour is produced.

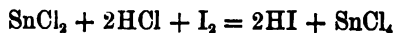
Repeat with the other flask. The two results should agree within 0.1 c.c. In titrating the second flask the amount of the solution required, up to the last c.c., may be run in at once, and the final reaction carefully determined.

In hydrochloric acid solution, the solution will be green after the titration (chromic chloride). It should be quite clear. If any turbidity appears during titration, there is a deficiency of free acid, and the assay must be rejected. The solution should not be too cold, as the reaction is not quite instantaneous. A temperature of from 20° to 30° C. is suitable.

In using this process for the estimation of iron in ores containing organic matter, iron pyrites, and sulphides of heavy metals, such as lead, copper, zinc, etc., the solution is liable to go back after completion, and on standing to again give a blue colour, especially if hot. This is due to the reducing action of these bodies on the ferric salt produced, and it tends to yield high results. This may be overcome by diluting the solution before titration, and using only slightly warm solutions. The insoluble matter should be filtered off through a small filter, and thoroughly washed before titration, if accurate and uniform results are to be obtained.

STANNOUS CHLORIDE AND IODINE METHOD.

For this purpose the iron must be in the ferric state. The reaction taking place being $\text{Fe}_2\text{Cl}_6 + \text{SnCl}_2 = \text{SnCl}_4 + 2\text{FeCl}_3$. The disappearance of the yellow colour is an indication that the end of the reaction is near, and its completion may be indicated by use of the indicator given below, or an excess of stannous chloride may be added, the amount in excess being afterwards determined by the addition of standard iodine solution thus—



This method is tedious, but accurate, and avoids reduction.

Standard Stannous Chloride Solution.—Dissolve 17 grms. of pure stannous chloride in water with an addition of about 5 c.c. hydrochloric acid, and dilute to a litre. Add some fragments of granulated tin, and keep in a well-stoppered bottle.

Or dissolve 11 grms. of pure tin in 100 c.c. strong hydrochloric

acid (the addition of a little platinum foil helps this to take place more readily), and dilute to a litre.

Standard Iodine Solution.—Dissolve 10 grms. of iodine in a solution of 40 grms. potassium iodide, and dilute to a litre.

Starch Solution.—0.5 gm. of starch, ground up in cold water, is added to 300 c.c. of boiling water, and boiled for a few minutes.

Standardizing.—It will first be necessary to determine the value of the stannous chloride solution as compared with the iodine solution.

Measure off 5 c.c. of stannous chloride accurately into a beaker, dilute to 50 c.c., and add a little starch solution. Then cautiously run in the iodine solution from a burette till the blue colour of iodide of starch is permanent. Read burette, and calculate, *e.g.* 5 c.c. SnCl_2 solution required 16.5 c.c. of iodine solution.

$\frac{16.5}{5} = 3.3$, *i.e.* 1 c.c. of stannous chloride solution is equivalent to 3.3 c.c. of iodine solution. This should be marked on the bottle.

To determine the iron value of the solution of tin chloride, proceed as follows:—

Dissolve 2 samples of 0.5 gm. pure iron in hydrochloric acid, add a crystal or two of potassium chlorate, and evaporate with more HCl if necessary, till chlorine is completely expelled. Use starch paper, *i.e.* filter paper, wetted with starch and potassium iodide, to test vapour if uncertain. Free chlorine liberates iodine, and turns the paper blue. Dilute to 50 c.c. Heat to boiling, and into the boiling solution run the tin chloride from a burette. As the addition proceeds the colour of the solution becomes lighter, and ultimately disappears. Then add about 1 c.c. of the tin chloride in excess. Let the solution cool, add a little starch, and titrate back with iodine till a blue colour is obtained to determine the excess. Multiply the volume of iodine solution required by the factor necessary to convert it into tin chloride, and deduct that amount from the volume of tin chloride employed, *e.g.* in titrating 0.5 gm. of iron.

Tin chloride taken	55 c.c.
Iodine solution	3.4
1 c.c. of tin chloride =	3.3 iodine
3.4 iodine	$= \frac{3.4}{3.3} = 1.02$ c.c. tin chloride solution
55 - 1.02	= 53.98 c.c. = 0.5 gm. Fe
1 c.c. of tin chloride =	$\frac{0.5}{53.98} = 0.00926$ gm. iron.

Standardization must be repeated for each batch of determinations.

In using this process care must be taken that all the iron is in the

ferric state. If oxidation is necessary, excess of the reagent used must be avoided, or the results will be high. Always work with hot solutions; do not titrate too hurriedly, and keep the iron solution fairly concentrated.

Estimation of Iron by Stannous Chloride and an Indicator.—In order to avoid titrating back with iodine, an indicator may be employed to render the presence of the slightest excess of tin chloride visible. The indicator employed is a solution of mercuric and platinic chlorides.

It is made by dissolving 0.5 grm. of platinic chloride and 40 grms. of mercuric chloride in a litre of water. A trace of stannous chloride is sufficient to produce a grey precipitate in a boiling solution. The tin chloride solution is prepared as before.

In standardizing, the solution of iron is titrated boiling, with an addition of 10 c.c. of the above solution. When the finishing point is reached a sudden darkening of the liquid takes place. The burette is then read.

Similar precautions to those used in the ordinary method must be taken.

Examples of Iron Estimations.—**Estimation of Iron in Red and Brown Hematite, Spathic Iron Ore, etc.**—Finely powder the mineral, and sift through at least an 80 sieve. Weigh out two quantities of 0.5 grm. each into two conical flasks, add 20 c.c. strong hydrochloric acid to each, and place on hot plate till solution of the iron is complete (about 20 minutes' boiling should suffice). Reduce with zinc, as directed (p. 178), filter through glass wool (or paper) into a porcelain dish, and titrate with standard potassium bichromate solution. Permanganate may be used if, before reduction, the hydrochloric solution be evaporated with sulphuric acid till fumes of the acid are evolved and the solution diluted.

Estimation of Iron in Blue Billy, Burnt Pyrites, Purple Ore, etc.—Dissolve two samples, 0.5 grm., as before, in hydrochloric acid, dilute to 50 c.c., and saturate the hot solution with sulphuretted hydrogen gas to reduce iron and precipitate any heavy metals. Boil till sulphuretted hydrogen is expelled, filter off the clotted sulphur, and titrate with potassium bichromate.

Estimation of Iron in Clay Iron-stone and Blackband Iron Ore.—Weigh out two finely sifted samples of 1 grm. each. Transfer to flasks, and dissolve in hydrochloric acid as before. Dilute to 50 to 70 c.c., and filter off insoluble matter. Wash thoroughly with small quantities of hot water. Add ammonia and ammonium sulphide in slight excess. Heat to boiling, and cautiously add hydrochloric acid to excess. The whole of the iron will now be in the ferrous state. Keep covered, and boil off

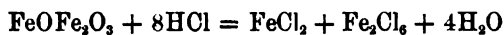
sulphuretted hydrogen. Filter off the precipitated sulphur, and titrate with potassium bichromate. This method gives excellent results in the presence of organic matter, etc., *e.g.* blackband ore, but it gives soluble iron only. Total iron, including that as pyrites, silicate, etc., is estimated by calcining a sample, say 10 grms., on a porcelain dish or scorifier at a red heat for 30 to 40 minutes in the muffle, and re-weighing. The loss in weight is noted, and two samples of the calcined ore are weighed and fused with 4 to 5 times their weight of bisulphate of potash in a platinum crucible. The melted mass is extracted with hydrochloric acid. All the iron is obtained in a soluble form, and the reduction may be proceeded with as before, or reduction with stannous chloride, zinc, etc. (see p. 173), may be resorted to.

Estimation of Iron in Tap Cinder.—Finely powder and sift the slag. Take two samples 0.5 grm. each. Fuse each in a platinum crucible with four times its weight of potassium bisulphate. Boil out the melted mass with hydrochloric acid and evaporate to small bulk. Reduce with sodium sulphite or other reducing agent, and titrate with potassium bichromate or permanganate.

Another Method for Iron Slags.*—Mix the weighed sample with about its own weight of pure fluor spar (free from iron) in a platinum crucible by means of a drawn-out glass rod. Clean the end of the rod in a little more fluoride, and add it to the contents of the crucible. Add strong hydrochloric acid, and heat on water bath till solution of the iron is complete. Reduce with zinc, and titrate with permanganate or bichromate.

Determination of Ferrous and Ferric Iron in Magnetite, etc.—Two samples are dissolved in hydrochloric acid, reduced by zinc, and total iron estimated with potassium or bichromate.

Two other samples are dissolved in flasks provided with Bunsen valves (see p. 173), as there directed, and titrated direct for ferrous iron only. The difference between the two results gives the ferric iron. It is obvious that when ferrous oxide or other ferrous compound is dissolved out of contact with air or other oxidizing agent, that the ferrous salt is produced, thus—



Determination of Ferric and Ferrous Iron in Refractory Ores or Slags.—The above method * may be employed to determine the amounts of ferrous and ferric iron, if the solution be conducted in an atmosphere of hydrogen, coal gas, or carbon dioxide. This can be done by standing the crucible on a small glass tripod in a large evaporating dish

* Wilbur and Whittlesey.

containing water, heated to about 90° to 95° C., inverting a beaker over it, and providing two bent tubes, one for conveying the gas into and the other from the beaker. The ferrous oxide may be thus determined in one sample, and the total iron after reduction in another (Fig. 74).

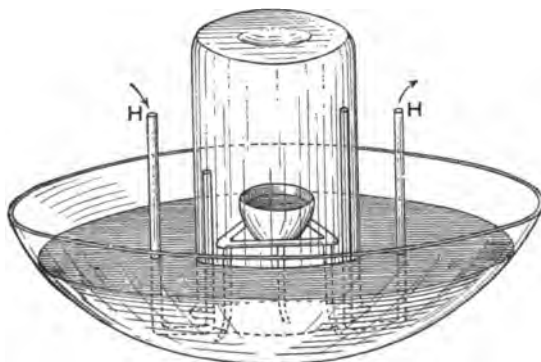


FIG. 74.

Estimation of Iron in Pig Iron, etc.—Weigh out two samples of 0.5 gm. of pig iron drillings, add 20 c.c. hydrochloric acid, and dissolve in covered beakers (No. 4) on hot plate. When action has completely ceased, add a little powdered potassium chlorate and evaporate carefully till chlorine is completely expelled (test with iodized starch paper), adding more hydrochloric acid if necessary. Heat to boiling, and estimate iron with standard stannous chloride by either of the methods given on pages 179, 180.

Estimation of Iron in Copper.—See p. 310.

NICKEL AND COBALT.

THESE metals frequently occur, associated in the same ores and products, although often only one of the metals is present.

The substances which most commonly come under the notice of the assayer are—

1. Ores of nickel and cobalt.
 - (a) Sulphides, arsenides, and arseniates.
 - (b) Silicates, oxides, and carbonates.
2. Mattes and speiss.
3. Blister copper.
4. Slags and smalts.
5. Vat liquors.
6. Alloys, with copper, iron, and other metals.

Ores of Nickel.—**Kupfernickel**, copper nickel, so-called on account of its coppery colour, a pale copper-red mineral, with a brownish-black streak. It is brittle, has a hardness of 5 to 5.5, and a sp. gr. of 7.3 to 7.6, and is a nickel arsenide, NiAs , containing, when pure, 44.1 per cent. of nickel. Iron, cobalt, antimony, and sulphur are often present. It is soluble in aqua regia, and before the blowpipe, yields arsenical fumes and fuses to a globule. The globule, heated in borax in oxidizing flame, yields reactions for iron, cobalt, and nickel in succession, the bead being first coloured yellow, then greenish and blue, and finally dark brown.

Chloanthite, white nickel, is tin-white in colour, with a grey-black streak. Hardness 5.5 to 6, and sp. gr. 6.4 to 6.7. Its composition is NiAs . Cobalt is generally present in considerable quantity. Before the blowpipe it behaves like kupfernickel.

Antimonial nickel resembles kupfernickel. It often contains lead.

Millerite, Capillary pyrites has a brass or bronze-yellow colour. It occasionally occurs crystallized in rhombohedra, with a perfect rhombohedral cleavage, but usually in delicate hair-like crystals, and sometimes in tufted crystalline incrustations, the outside of which are apple-green and earthy, on account of oxidation. It is brittle; hardness, 3 to 3.5 (distinction from iron and copper pyrites), sp. gr., 4.5

to 5.6. It consists of nickel sulphide, NiS , and contains 64.9 per cent. of nickel. Iron, copper, and cobalt are often present.

Emerald nickel occurs as an emerald green incrustation, with a pale green streak. Hardness, 3 to 3.25; sp. gr., 2.5 to 2.6. It is a hydrated carbonate of nickel, and occurs associated with chrome iron and serpentine. It gives the usual nickel reactions, and is soluble in hydrochloric acid.

Annabergitē is a basic arsenate of nickel, which forms an incrustation (often in patches) on arsenical nickel ores. It is apple-green in colour, and soft.

Garnierite is a green (light or dark) mineral with a talcose lustre and feel. It may be earthy in character, with a hardness of 2-3.5, and sp. gr. 2.3-2.8, and often the green colour is masked by the presence of ferric hydrate. It consists of a hydrated double silicate of nickel and magnesia, often containing iron. It is found extensively in New Caledonia, associated with serpentine and soapstone. It gives the nickel reaction with borax.

Many ores of other metals contain nickel. Pyrrhotine (magnetic iron pyrites), chalcopyrite (copper pyrites), and other copper ores, and mispickel may be mentioned. The famous nickel ore of Sudbury (Canada) is a pyrrhotine containing a small percentage of nickel.

Cobalt Ores.—**Smaltine**, tin-white cobalt, is a tin-white to steely grey mineral, which occurs massive and less often in crystals belonging to the cubic system. Tarnish sometimes gives it an iridescent appearance. The lustre is metallic, and the streak greyish black. It is brittle, breaking with a granular fracture. Hardness, 5.5 to 6; sp. gr., 6.4 to 7.2. Its composition is CoAs_2 , and when pure contains 26 per cent. of cobalt, but nickel and iron often replace the cobalt. It seldom contains more than 23 per cent., and generally much less.

It yields arsenical fumes when heated before the blowpipe, and a globule which, when heated in borax in oxidizing flame, gives successive reactions of iron, cobalt, and nickel. Heated in a closed tube, it yields an arsenical mirror.

Cobaltine is a sulpharsenide of cobalt, CoS_2CoAs , which closely resembles smaltine, but does not yield an arsenical mirror when heated in a closed tube.

Cobalt-bloom, erythrite, is a rose or peach coloured mineral, occurring in crystals and as an incrustation. The crystals cleave perfectly. Hardness, 1.5 to 2; sp. gr., 2.95. It is a hydrated arseniate of cobalt. It dissolves in hydrochloric acid, and gives the blue bead with borax.

Earthy cobalt, asbolan, is an earthy black mineral, consisting of oxides of cobalt, manganese, copper, etc.

Cobalt, like nickel, occurs in small quantity in minerals of other metals.

Mattes and Speiss.—**Mattes** (sulphides), produced in copper smelting and nickel smelting, may contain from less than one per cent. to 50 per cent. or even more of the metals.

Speiss (arsenides), produced in separation of the metals from copper ores and in smelting arsenical ores, are arsenides of nickel and cobalt, with iron and copper. The fracture resembles smaltine.

Smalts.—A blue silicate of cobalt manufactured for colouring purposes.

Vat Liquors.—The liquors left from the electro-refining of copper often contain nickel and cobalt. As the blister copper is dissolved and deposited, any nickel and cobalt remain in solution.

Alloys.—German silver, white copper, and nickel steel are the alloys which most commonly come under the assayer's notice.

REACTIONS FOR NICKEL AND COBALT.

Nickel.—Nickel, like iron, forms two classes of salts—nickelous and nickelic. The former are usually green, but become yellow when dehydrated. The nickelic salts are unstable and of little importance. The metal dissolves in hydrochloric acid, yielding nickel chloride, NiCl_2 .

1. Sulphuretted hydrogen in hydrochloric acid solution gives no precipitate.

2. Ammonia gives a precipitate, which dissolves in excess, yielding a blue solution (compare Copper). Reprecipitated by NaHO .

3. Caustic soda, on boiling, gives an apple-green precipitate, insoluble in excess, but soluble in ammonium salts.

4. Ammonium sulphide in alkaline solutions yields a black precipitate somewhat soluble in excess, yielding a brown solution, best seen on filtration. Expulsion of the ammonium sulphide by boiling, or addition of slight excess of hydrochloric or other acid, precipitates the dissolved sulphide. The precipitate is insoluble in cold dilute hydrochloric acid, and also in acetic and dilute nitric acids.

5. Sodium hypochlorite, bleaching powder, and some other oxidizing agents, precipitate black nickelic hydrate, $\text{Ni}_2\text{H}_2\text{O}_6$. Iodine does not produce this oxidation.

6. Potassium cyanide, in neutral solutions, precipitates nickel cyanide soluble in excess, with formation of a double cyanide. On adding sodium hypochlorite or other oxidizing agent in considerable excess to

the solution and boiling, the cyanide is decomposed, and the black hydrate of nickel is precipitated (see Cobalt).

7. Sodium carbonate precipitates a basic carbonate of nickel.

Dry Reactions.—With fusion mixture on charcoal in the reducing flame, nickel salts yield a black magnetic mass.

Heated in borax in the oxidizing flame, nickel salts yield a sherry-brown bead. In the reducing flame the bead is colourless or grey, owing to reduction of the nickel.

Cobalt.—Cobalt, like nickel and iron, also forms two classes of salts—cobaltous and cobaltic. The former are the more important. The corresponding oxides are CoO and Co_2O_3 . Cobaltous oxide is black, but its salts are pink when hydrated and blue when anhydrous. In the evaporation of pink solutions, a change to blue when nearly dry indicates cobalt.

1. Sulphuretted hydrogen in hydrochloric acid solution yield no precipitate.

2. Ammonia yields a blue precipitate, which dissolves in excess, giving a brownish solution.

3. Caustic soda precipitates CoH_2O_2 , insoluble in excess, but soluble in ammonium salts.

4. Ammonium sulphide in alkaline solutions throws down cobalt sulphide, CoS , resembling NiS in its insolubility in acids.

5. Oxidizing agents precipitate the hydrated oxide, CoH_2O_2 . Iodine produces the oxidation. Compare nickel.

6. Potassium cyanide added in excess to a slightly acid solution forms, on boiling, a double cyanide, $\text{K}_3\text{Co}(\text{CN})_6$, potassium cobalticyanide, which is very stable. On boiling the solution with oxidizing agents it is not decomposed, and no black precipitate falls. (Compare nickel.)

7. Potassium nitrite in acetic acid solution precipitates, on standing, yellow crystalline $\text{Co}_2\text{O}_3, 3\text{N}_2\text{O}_5, 6\text{KNO}_3, 2\text{H}_2\text{O}$. This reaction is taken advantage of in the quantitative separation of the metal.

8. Potassium ferricyanide in a solution containing citric or tartaric acid gives a dark-red coloration. This test is very delicate.

Dry Reactions.—Cobalt salts heated before the blowpipe on charcoal in the reducing flame yield a black mass, which is only very faintly magnetic.

Earthy phosphates and alumina are coloured blue by cobalt oxide, and zinc oxide green.

With borax, cobalt yields a deep blue bead, both in the oxidizing and reducing flames. This may be masked by the presence of other oxides.

DRY ASSAY OF NICKEL AND COBALT.

In this assay advantage is taken (1) of the facility with which nickel and cobalt may be concentrated in combination with arsenic to form a speiss; (2) of the order of oxidation of the metals which the speiss may contain, viz. iron, cobalt, nickel, and copper, and the colours they impart to borax. They are removed in the order named. Iron communicates a brownish colour to borax, cobalt a blue, nickel a sherry-brown, and copper a blue. Hence, on submitting the speiss to scorification in contact with borax, the colour imparted by the oxide produced indicates the metal being removed. By careful and frequent examination of the colour resulting and the renewal of the borax, it is possible to hit upon the point at which first the iron and then the cobalt and nickel are removed, in succession. A greenish tint is imparted to the borax at the moment the cobalt begins to scorify, succeeded by a full blue (with fresh borax), followed by a greenish tint when the nickel commences to pass out. This changes to the full sherry-brown, and is succeeded by a greenish tint when copper commences to oxidize.

Careful examination and much care are necessary to obtain even fair results. By weighing the button at the various stages, the proportion of its constituents may be determined. If copper be present, 1 grm. of gold is added to the button after the removal of the cobalt.

Assay of Ores and Speiss Free from Copper.—From 5 to 25 grms. of the ore are finely powdered and passed through an 80 sieve and calcined "sweet." At the end of the roasting some finely ground anthracite must be added, and the calcination continued till this is burnt away, thus ensuring the reduction of sulphates and arsenates formed in the earlier stages.

The roasted mass is mixed with $\frac{1}{2}$ to $\frac{1}{2}$ its weight of arsenic, its own weight of carbonate of soda, 5 grms. of argol, and 2 to 4 grms. of borax, run down in a crucible at a moderate temperature, and, when in a state of quiet fusion, poured. If iron be absent from the assay, 0.5 grm. of pure iron filings or wire, cut into small pieces, must be added before fusion.

Or, the ore after roasting may be heated with its own weight of arsenic in a covered crucible, and then run down with a mixture of carbonate of soda, argol, and borax, with a little arsenic.

When cold, the button is detached from the slag and carefully weighed. It should be metallic-looking, and have a smooth grey surface. Portions weighing 1 grm. should be taken for the subsequent scorification.

Examination of Speiss.—The scorification with borax is conducted in small shallow dishes, $\frac{3}{4}$ inch in diameter inside and $\frac{1}{8}$ inch deep (Fig. 75).



FIG. 75.

These may be made in the laboratory of finely-sifted clay and ground pots. The clay should be stiff, and as much pressure as possible used in shaping them. The die (A, Fig. 76) may be made of boxwood, and provided with a gun metal or iron ring, B. The dishes should be dried carefully and heated to dull redness in a muffle before use.

While preparing the speiss, a small muffle should be made as hot as possible, as the success of the operation depends largely on the temperature. The back of the muffle should be white hot. Place a number of the small dishes in the muffle. Have at hand some ground borax glass, and a vessel of cold water. Put about a gramme (rather less than

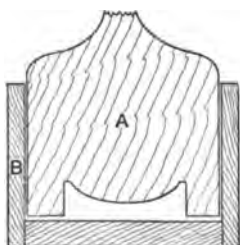


FIG. 76.

more) of borax in one of the dishes as far from the front as can be seen. It is convenient to wrap the borax in tissue paper and drop it in with the tongs. When the borax is melted and fully heated, drop in the speiss, also wrapped in tissue paper.

The muffle should be hot enough to melt the speiss immediately, or the order of oxidation will not be preserved. The borax should not be sufficient to cover the speiss when melted.

For a moment the surface is dull, but almost instantly brightens and scorifies, very much like the brightening stage in the cupellation of silver. In a few moments remove the dish and contents, and immediately place the bottom of it in water to cool it, and, as soon as the bead is solid, submerge it in the water.

Examine the slag. If iron only has passed off, the brownish-yellow tint due to that metal will only be observed, but if the smallest amount of cobalt has been removed, the slag will be greenish, or, if a larger quantity, blue.

The correct stage has been reached when a faint green tinge is visible in the slags near the edge and round the button.

If this be not observed, the operation is repeated till the point is arrived at. If it is overstepped, the scorification is restarted with a fresh portion of speiss.

The speiss now only contains cobalt, nickel, and copper. It is weighed, and the operation repeated with every precaution till the cobalt is removed. Less borax is necessary as the bead is reduced in size, and a green cap (of arsenate) appears when the nickel commences to oxidize, as well as the greenish tinge in the slags near the button. The attainment of this point is marked also by the motion of the button momentarily ceasing. The process needs very careful watching. The dish is withdrawn, and quenched carefully as before. If, on examination, it is doubtful whether the nickel has commenced to scorify, it is best to weigh the prill and return it momentarily to a scorifier with fresh borax, and examine immediately it is melted. The dense blue of the cobalt will not then interfere, and the brownish colour of the nickel (and the green cap) will be apparent. The prill is weighed. If copper were present in the speiss, the prill will now consist of nickel and copper arsenides. If much nickel is present, the scorification may be further proceeded with in the same manner, but it is better to at once add 1 grm. of pure gold, and continue the scorification so long as nickel continues to be removed. The resulting bead consists of the added gold and copper. It is weighed, and the increase in weight of the gold bead gives the copper. Confirmatory results may be obtained by cupelling the gold-copper bead with 34 times its weight of lead, when the gold only will be left, the loss of weight being copper.

NOTE.—In the above remarks it has been assumed that cobalt is present. If it is absent, it is difficult to ascertain the point at which iron is removed and nickel commences to pass out. Further, in assaying an unknown speiss, which may contain nickel and iron only, the green arseniate of nickel which forms on the surface and under the bead must not be confounded with the green tinge indicated above.

Modified Method.—Some assayers, in order to avoid the difficulty caused by the copper, remove it before forming the speiss.

The sample of ore is digested with aqua regia till completely decomposed, hydrochloric acid added, and the nitric acid expelled by evaporation. Water is then added, and the liquor saturated with sulphuretted hydrogen, which precipitates the copper, etc. The liquid is filtered, and the residue washed with water containing sulphuretted hydrogen.

The filtrate is then boiled till sulphuretted hydrogen is completely expelled, peroxidized by adding a few drops of nitric acid to the boiling solution and neutralized. To the neutral solution barium carbonate is added in excess and well shaken. The solution is filtered, and the precipitate washed, dried, and ignited. This precipitate, which contains the whole of the iron cobalt and nickel, is converted into a speiss as before, but without roasting.

Statement of Results.—

Weight of ore taken = 20 grms.	
Weight of speiss obtained = 3.253 grms.	
Weight of speiss taken for scorification = 1 gm.	
„	„ after removal of iron = 0.7258 gm.
Weight of Fe_2As = 0.2742	
„	„ „ „ cobalt = 0.5196 gm.
Weight of Co_2As = 0.2062.	
„	gold added = 1.5 gm.
„	gold + copper = 1.62 „
= Cu = 0.12.	

But copper is present as Cu_3As .

$$\text{Cu} = 63.5, \text{As} = 75. \quad \text{Cu}_3\text{As} = (63.5 \times 3 + 75) = 265.5.$$

$$\therefore \frac{0.12}{190.5} \times 265.5 = 0.1672 \text{ Cu}_3\text{As}.$$

$$\text{Weight of Ni}_2\text{As} + \text{Cu}_3\text{As} = 0.5196, \text{Cu}_3\text{As} = 0.1672.$$

$$\therefore \text{Weight Ni}_2\text{As} = 0.3524.$$

Calculation of per centage of cobalt.

$$\text{Weight of Co}_2\text{As in speiss scorified} = 0.2062.$$

But only 1 gm. out of 3.253 was taken.

$$\therefore 0.2062 \times 3.253 = 0.670768 = \text{Co}_2\text{As in 20 grms. of ore originally taken, and}$$

$$20:100 :: 0.670768:\text{per cent. of Co}_2\text{As (or equivalent) in ore} \\ = 3.3539 \text{ Co}_2\text{As}.$$

$$\text{Co} = 58.8, \text{As} = 75.$$

$$\therefore \text{Co}_2\text{As} = (58.8 \times 2) + 75 = 192.6, \text{ from which Co}_2\text{As contains} \\ \frac{117.6}{192.6} \text{ of cobalt.}$$

$$\therefore 3.3538 \times \frac{117.6}{192.6} = 2.04779 \text{ per cent. Co.}$$

Calculation of percentage of nickel.

Weight of Ni_2As = 0.3524. Then, on the same reasoning—

$$\therefore 0.3524 \times 3.253 = 1.1464 = \text{Ni}_2\text{As in 20 grms. ore.}$$

$$\therefore 20:100 :: 1.1464:\text{per cent. Ni}_2\text{As (or equivalent) in ore} \\ = 5.732 \text{ Ni}_2\text{As}.$$

$$\text{Ni} = 58.8, \text{As} = 75.$$

$$\text{Ni}_2\text{As} = (58.8 \times 2) + 75 = 192.6, \text{ from which Ni}_2\text{As contains} \\ \frac{117.6}{192.6} \text{ of nickel.}$$

$$5.732 \times \frac{117.6}{192.6} = 3.4997 \text{ per cent. Ni.}$$

NOTE.—Factor for Ni and Co in Ni_2As and Co_2As = 0.61059.

Assays of speiss are conducted in the same manner. If no iron be present, some must be added, as in assaying ores.

WET ASSAY OF COBALT AND NICKEL.

This assay is generally complicated by the presence of cobalt and often antimony, iron, and arsenic, while manganese and zinc are frequently present. A consideration of the chemical reactions of these metals will afford some idea of the difficulties thus introduced.

Assay of Arsenical and Sulphurous Ores.—From 1 to 5 grms. of ore is placed in a porcelain evaporating dish and carefully roasted to expel sulphur and arsenic, finishing at a red heat. The residue, after cooling, is moistened with a strong solution of sugar, or mixed with a few grains of charcoal powder, and the roasting is continued till sulphur and arsenic can no longer be detected, and the carbon is removed, the charge being stirred with a glass or porcelain rod. The residue in the dish is treated with hydrochloric acid, small additions of nitric acid or potassium chlorate being made from time to time. When solution is complete, the liquid is evaporated to small bulk to expel acid, diluted with water, and any insoluble matter filtered off. (If the residue is dark-coloured, the liquor is decanted, and the residue dried, re-roasted, and again treated with acid. This is seldom necessary if the first roasting is carefully conducted.)

If the solution does not contain iron, some ferric chloride must be added. The filtrate is then neutralized with ammonia or sodium carbonate, excess of acetate of soda or ammonia (from 10 to 40 grms.) added, and the liquid boiled. By this means the iron, alumina, arsenic (and phosphoric acid, if present), are precipitated. The precipitate is filtered and washed—a long and tedious operation at best. By using cellular paper, sodium sulphate in the wash water, and washing as much as possible by decantation, it may be curtailed; but an equally good result may be obtained, especially if the precipitate is a large one, by diluting the liquid after precipitation to half a litre or a litre, and filtering off one half, *i.e.* 250 or 500 c.c., as the case may be, through a dry filter paper. This obviates all washing, etc. If much iron is present it is sometimes convenient to effect the precipitation of the bulk of that metal free from nickel and cobalt by nearly neutralizing with ammonia in presence of much ammonium chloride, adding a dilute solution of ammonium carbonate till a faint precipitate is produced, and then boiling. The iron is precipitated as a basic salt. The remaining iron is precipitated in the filtrate by boiling with ammonium acetate.

The filtrate, faintly acid with acetic acid, is warmed, and saturated with sulphuretted hydrogen. This precipitates copper, nickel, cobalt, zinc, and leaves the manganese, calcium, barium, etc., in solution. After settling for some hours, the clear liquor is decanted through a filter, and the precipitate washed by decantation with boiled water containing sulphuretted hydrogen, till free from acetates. The precipitate on the filter is then washed back into the beaker, and the water boiled off, or, the precipitate may be dried and detached from the paper, which is afterwards burnt and the ash added. The precipitate is heated with strong hydrochloric acid, additions of potassium chlorate being made till solution is complete, or aqua regia may be used to effect solution.

After boiling to expel chlorine, the solution, which must be slightly acid, is diluted to 100 c.c., warmed, and saturated with sulphuretted hydrogen. This precipitates the copper as sulphide, which is filtered off and washed. The filtrate is tested for copper by again passing sulphuretted hydrogen. When free from copper it is boiled to completely expel sulphuretted hydrogen neutralized with ammonia till a slight precipitate forms, and then acidified with acetic acid. On passing a slow stream of sulphuretted hydrogen through the *cold* solution, any zinc present is thrown down, as the white sulphide, and if the operation be carefully conducted the zinc may be completely removed. Immediately any darkening occurs, arrest the current of gas. After standing, the precipitate is filtered off. The solution containing the nickel and cobalt is then treated by one of the following methods:—

(a) The solution is exactly neutralized and the nickel and cobalt precipitated with potassium binoxalate, the former as double, and the latter as simple oxalate. The precipitate is ignited in an open crucible, the nickel remaining as NiO and the cobalt as Co_3O_4 . After ignition, the residue must be washed by decantation with a few drops of water, to remove potassium carbonate resulting from the decomposition of the oxalate before weighing.

(b) The nickel and cobalt are obtained as sulphates by evaporation to dryness with sulphuric acid in a weighed capsule. In this case the sulphide precipitate must be dissolved without the addition of potassium chlorate, so that the solution after separating zinc only contains ammonium salts in addition to the nickel and cobalt.

(c) The nickel and cobalt may be precipitated as hydrates by caustic potash. In this case pure potassium or sodium carbonate must be employed to neutralize the solution before separating zinc, or the precipitation will be incomplete. This precipitate is, however, very slimy and difficult to filter. The nickel in the precipitate after ignition exists as NiO, and the cobalt as Co_3O_4 .

(d) The solution may be made alkaline with ammonia and sulphuretted hydrogen employed to precipitate the metals, and the precipitate converted into sulphate by carefully treating the dried precipitate and paper ash in a weighed capsule with nitric acid till completely oxidized, and then adding sulphuric acid, and evaporating to dryness, to expel the excess of acid.

Or, the liquor after filtering off the sulphide of copper is nearly neutralized with soda, a little sodium acetate added, and a few drops of acetic acid. It is then heated to boiling, and saturated with a rapid stream of sulphuretted hydrogen. By this means, nickel, cobalt, and zinc are precipitated as sulphides, manganese remaining in solution. After standing aside till settled, the clear liquor is decanted and the precipitate washed by decantation with freshly boiled water. Any precipitate on the filter is washed back into the beaker, using as little water as possible. The assay is then evaporated just to dryness, the beaker covered with a clock-glass, and the precipitate dissolved by boiling aqua regia. Water is added to dilute the solution greatly, and excess of acid nearly neutralized by soda. The liquid is heated to boiling. Sodium hypochlorite or hypobromite is then added in considerable excess. The nickel and cobalt are precipitated as hydrated sesquioxides, and may be filtered, dried, ignited, and weighed.

Factors : see table of factor in Appendix.

For separation from cobalt, see p. 195.

NOTES.—1. In assaying ores zinc and manganese may be got rid of by roasting a weighed sample and fusing it with sodium carbonate, potassium carbonate, arsenious oxide, and charcoal, or with black flux, potassium cyanide, and arsenious oxide. Nickel and cobalt, with copper and iron, form a speiss, while the zinc and manganese are removed in the slag. See Dry Assay of Nickel.

2. A simple, but not very accurate, method of removing zinc is to make the solution alkaline, after removing copper, and saturate with sulphuretted hydrogen. The precipitate is collected on a filter, washed, and then washed down into a 300 c.c. flask, with *boiled* water, about 5 to 10 c.c. of hydrochloric acid added, the flask filled with boiled water, and stoppered. It is then set aside for some hours, with occasional shaking. By this means the zinc sulphide is dissolved. The solution is decanted. The residue rapidly washed with boiled water, and treated as above to determine the nickel and cobalt.

Method of estimating Nickel and Cobalt in Ores not containing Manganese.—The ore is dissolved in aqua regia with or without previous roasting, and evaporated to dryness. The residue is taken up with hydrochloric acid, diluted, and the hot liquor saturated with sulphuretted hydrogen. If arsenic be present, sodium sulphite or sulphurous acid is previously added to reduce the arsenic acid, and SO_2 boiled off. The precipitated sulphides of arsenic, copper, bismuth, and lead are filtered off, washed, the filtrate boiled to expel sulphuretted hydrogen, and nitric acid added to peroxidize the iron. The

solution is nearly neutralized with sodium carbonate, and the iron removed as basic acetate (see p. 351). The filtrate from the iron precipitate is treated with sodium hypochlorite, chlorine water, or bromine, and made alkaline with caustic soda. This throws down the nickel and cobalt, together with some zinc. After boiling till the precipitate is black, it is filtered off, washed and dried. The precipitate is placed in a porcelain boat, the filter ash added, and reduced to metal by heating in a current of hydrogen. The cobalt and nickel may then be separated as directed on p. 195.

Or, the precipitate may be dissolved and the metals precipitated as oxalates or converted into sulphates.

Estimation of Nickel by Electrolysis.—This method is only useful for estimating nickel in solutions free from other metals. Such as are obtained in the analysis of nickel alloys, after the removal of the copper, iron, and zinc, by the usual methods. The nickel solution (preferably in nitric acid) is made strongly alkaline with ammonia, some ammonium nitrate added, and electrolyzed as described under copper. A higher electromotive force is, however, necessary, and 3 Daniell or 2 Bunsen cells must be used, coupled in series, *i.e.* zinc of one cell to copper of the next cell, the end zinc and copper being joined to the platinum electrodes. The liquor is kept at about 70° F., and the current passed for 12 hours. The residual liquor should smell of ammonia, be free from blue colour, and yield no brown discoloration or precipitate with ammonium sulphide. If it does not smell strongly of ammonia, some must be added before rejecting it.

The nickel is deposited as a bright film, and may be washed with water and alcohol, dried and weighed. (See Copper, p. 92.)

Alloys containing copper, nickel, iron, and zinc, are most easily dealt with by this method.

The alloy is dissolved in nitric acid, and the copper estimated electrolytically, as on p. 92. If the solution after electrolysis be not free from copper, it is saturated with sulphuretted hydrogen, the precipitate collected, and the copper it contains estimated colorimetrically. The filtrate is then boiled to expel sulphuretted hydrogen, nitric acid added, the iron precipitated by ammonia, filtered off and washed. If much iron be present, this precipitate must be dissolved and reprecipitated. If zinc be absent, the solution may be electrolyzed for nickel at once; but, in presence of zinc, the alkaline solution must be saturated with sulphuretted hydrogen, and the precipitate collected, and washed with water containing sulphuretted hydrogen dissolved in nitric acid, large excess of sodium hydrate added, the solution boiled, and the precipitate filtered off and washed. The zinc, to a large extent, remains in solution

and is thus removed. The precipitate is dissolved in nitric acid, made alkaline with ammonia, and electrolyzed. The removal of the zinc need not be complete.

Or, the alkaline solution containing the nickel and zinc may be boiled with bromine water. By this means the nickel is precipitated as black hydrated sesquioxide, which may be readily filtered. This is redissolved, and treated by electrolysis.

Assay of Nickel in Pyrites and Mattes.—2 to 5 grms. of the matte is dissolved in aqua regia and evaporated to dryness. The residue is taken up with hydrochloric acid, and copper and other metals precipitated by sulphuretted hydrogen, filtered off and washed. The solution is boiled to expel sulphuretted hydrogen, the iron peroxidized with nitric acid, a strong solution of ammonium phosphate added, equal to about 10 grms. of the salt, after which the iron is precipitated by ammonium acetate (see above). It is necessary that the solution should contain a fair amount of acetic acid. The iron precipitate is filtered off and washed with weak acetic acid. The filtrate is heated to boiling, caustic potash added in slight excess, and the solution boiled till no smell of ammonia is observed. The nickel is precipitated as phosphate, which is filtered off and washed, dissolved in weak sulphuric or nitric acid, and treated electrolytically as above.

COBALT.

This metal has been dealt with in conjunction with nickel, with which it is generally associated. The quantity in nickel minerals is generally small.

It is estimated by precipitation with potassium nitrite, or by oxidizing agents.

Estimation by Precipitation as Double Nitrite.—The mixed nickel and cobalt sulphides, metal, or other compounds, after separation from other metals, are dissolved in nitric acid or water, and caustic potash is added carefully till a precipitate forms. Acetic acid is then added in excess, and a strong solution of potassium nitrite. After standing 24 hours, the precipitated double nitrite of cobalt and potassium, $\text{Co}(\text{NO}_2)_2 \cdot 3\text{KNO}_2$, is filtered off, washed with solution of potassium acetate, afterwards with alcohol, and dried. The precipitate is detached from the filter, transferred to a weighed porcelain crucible, and cautiously heated with sulphuric acid. The excess of acid is expelled by careful heating, taking care not to heat too strongly. The residue is weighed. It consists of $3\text{K}_2\text{SO}_4 \cdot 2\text{CoSO}_4$, and contains 14.17 per cent. of cobalt.

Estimation of Cobalt by Precipitation with Oxidizing Agents.—

The mixed nickel and cobalt sulphides are dissolved in aqua regia, and the solution evaporated to expel most of the acid. Potassium cyanide is then added till the precipitate which forms is redissolved, and the solution is boiled for a few minutes. It is then diluted, heated to boiling, and large excess of freshly precipitated mercuric oxide* added, boiled for some time, filtered, and washed. The precipitate, which consists of nickel oxide and cyanide, with the excess of mercuric oxide added, is dried, ignited, and weighed as nickel oxide. The filtrate contains the cobalt. It is precipitated by adding a solution of mercurous nitrate in excess to the solution. This throws down the cobalt as mercury cobalt-cyanide, which is filtered, dried, ignited, transferred to a Rose's crucible (p. 258), and ignited in a stream of hydrogen. The resulting metal is weighed.

NOTE.—The ignition must be carried out in a draught chamber with a powerful draught.

* Prepared by adding caustic potash to mercuric chloride, and boiling, the latter salt being in excess. It is allowed to settle, and washed by decantation before use.

MANGANESE.

THE substances in which manganese has most often to be determined are—

Manganese ores.
Weldon mud.
Slags.
Metallic alloys with iron and copper.
Steel.

Ores of Manganese. **Pyrolusite**, Black oxide of manganese MnO_2 .—The crystals are rhombic, but it generally occurs massive in various forms. The colour is black to steel grey, streak black. Lustre, sub-metallic or silky. Hardness, 2 to 2·5, rather brittle; sp. gr., 4·7 to 5. Gives manganese reactions, and evolves chlorine when heated with hydrochloric acid. **Polianite** in composition and general properties resembles pyrolusite, but its hardness is 6–6·5. **Varvacite** is a hydrated oxide, $\text{MnO}_2 \cdot 5\text{H}_2\text{O}$.

Hausmanite, Mn_3O_4 .—Crystals, tetragonal pyramids. Colour, iron black to brownish; streak brown. Opaque. Hardness, 5–5·5; sp. gr., 4·7–4·8. **Braunite**.—A siliceous variety, $3\text{Mn}_2\text{O}_3 + \text{MnOSiO}_2$, resembles hausmanite, but is browner and harder.

Psilomelane.—Non-crystalline, generally massive, reniform, or botryoidal, often with bright reniform surfaces. Colour, iron black or bluish black. Streak, brownish black, glistening. Lustre, dull to glimmering. Hardness, 5·5–6; sp. gr., 4·1–4·3. Gives flame reactions for barium, and often copper and potash. Yields chlorine with hydrochloric acid.

Wad.—Non-crystalline, massive, reniform, frothlike, also scaly and compact. Colour and streak, brownish to black. Hardness up to 3. Composition very variable, principally MnO_2 , but copper, cobalt, and other metals often present. Yields chlorine with hydrochloric acid, gives manganese reactions.

Manganite, Hydrated manganese oxide, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$.—Crystals rhombic, usually long, and in bundles or radiating groups. Cleavage perfect.

Colour, iron black, dark steel grey, or brownish; streak brown. Lustre, nearly metallic. Hardness, 3·5–4; sp. gr., 4·3–4·5. Brittle.

Diallogite, Rhodochrosite, Carbonate of Manganese, MnCO_3 .—Crystals rhombohedral, often with curved faces, also occurs massive in various forms. Colour, rose-pink and flesh-red. Brown when decomposed. Lustre, pearly. Translucent. Hardness, 3·5–4·5; sp. gr., 3·4–3·6. Effervesces with warm acid, and gives manganese reactions. Blackens before blowpipe. Infusible.

Rhodonite.—Generally massive. Colour, rose-pink or brownish. Translucent. Hardness, 5–5·5; sp. gr., 3·5–3·7. No effervescence with acid. Fusible. Gives manganese reactions.

Slags.—From the manufacture of spiegeleisen, ferromanganese, silico-manganese. These are usually green in colour, and may be glassy and strong. They contain up to 13 or 14 per cent. of manganese as manganate and as silicate.

Alloys.—**Spiegeleisen** has a brilliant crystalline appearance on fresh fractures. The crystal faces are smaller as the proportion of manganese increases. It may contain up to 30 per cent. of manganese.

Ferromanganese.—With more than 30 per cent. of manganese, the characteristic brilliant fracture is less evident, and with large proportions the fracture becomes finely granular. Often coloured bands are noticed, and occasionally masses of needle-shaped crystals. Up to 85 or 88 per cent. of manganese may be present.

Manganese Bronze.—Usually contains only traces of the metal.

Steel.—Mild steel may contain up to 1 per cent. Crucible cast steel usually contains not more than 0·2 or 0·3 per cent.

TESTS FOR MANGANESE.

Dry Tests.—Oxidized compounds heated on charcoal with fusion mixture yield a black non-magnetic mass.

Borax gives a colourless or grey bead in the reducing flame, and a violet, claret-coloured or amethyst bead in the oxidizing flame.

Fused with a mixture of nitrate and carbonate of soda, manganese compounds yield a green mass, containing manganate of soda. This is one of the most characteristic tests.

Wet Tests.—All the salts of manganese are soluble in water or dilute acids, consequently hydrochloric acid and sulphuretted hydrogen in acid solutions give no precipitates.

In neutral solutions ammonia precipitates white manganese hydrate, which rapidly absorbs oxygen, and darkens in colour. In presence of much ammonium chloride and other ammonium salts, the precipitate

is either not produced or redissolves. For this reason ammonium hydrate gives no precipitate in acid solutions, unless the solution be strong. On standing and exposure to the air, especially on boiling, brown $Mn_2H_2O_6$ is precipitated. Hence complete separation from the iron group cannot be obtained by simple precipitation with ammonia.

Sodium hydrate precipitates white manganous hydrate, which absorbs oxygen. The precipitate is not thrown down in the presence of tartaric acid and other fixed organic matter.

Ammonium sulphide, added to alkaline solutions, precipitates flesh-coloured manganese sulphide soluble in acetic acid. Sulphuretted hydrogen in alkaline solution, produces the same precipitate.

Sodium carbonate precipitates white manganese carbonate, insoluble in excess, but slightly soluble in ammonium salts.

Chlorine or bromine or hydrogen peroxide in neutral or acetic acid solutions, produces a black precipitate of $MnO_2, 2H_2O$.

Boiled with nitric acid and peroxide of lead, oxidized manganese compounds yield permanganic acid, which may be recognized by the violet colour of the solution on settling. This test is delicate.

ESTIMATION OF MANGANESE.

The methods adopted for the estimation of manganese in metals and alloys, and in minerals other than those used for the production of chlorine, depend on the insolubility of the carbonate in alkaline solution, and the precipitation of the hydrated peroxide by oxidizing agents in neutral solution; the preparation of the solution for this purpose being attended with the separation of the metals of the lead, copper, and iron groups.

Volumetric methods for its estimation, based on the oxidizing powers of permanganic acid, are also in use.

For the valuation of a manganese ore for chlorine making, estimation is made of its gas-generating power, as its value for this purpose depends, not on the amount of manganese, but on the amount of chlorine which can be evolved.

GRAVIMETRIC METHODS.

Estimation of Manganese in Ores.—0.5 to 5 grms. of the finely powdered mineral is digested with concentrated hydrochloric acid in a beaker, and carefully evaporated to dryness. More acid is then added, with a crystal or two of potassium chlorate (to destroy organic matter),

the solution again evaporated to complete dryness, and heated somewhat strongly.* When cool, water and dilute hydrochloric acid are added, heat applied, and the insoluble matter consisting mainly of silica filtered off. The solution is saturated with sulphuretted hydrogen while warm and the precipitate filtered off and washed. The filtrate is boiled with strong nitric acid to peroxidize iron, carefully neutralized with ammonia,† and sodium or ammonium acetate added in considerable excess, and boiled. The precipitated basic ferric and aluminium acetates are filtered off, and washed. The filtrate may contain Ni, Co, Zn, Ca, Ba, Sr, and Mn. It is tested for its freedom from iron, with potassium ferrocyanide on a spot plate, and then made alkaline with ammonia.

Precipitation of the Manganese.—**Method I.**—Ammonium sulphide is added in slight excess, and the precipitate filtered off and washed. The precipitate is heated with dilute acetic acid, filtered, and washed. The filtrate which contains the manganese is neutralized with caustic soda, and carefully precipitated with sodium carbonate. The precipitate of MnCO_3 is filtered, dried, ignited strongly, and weighed as Mn_2O_3 . It contains 72.05 per cent. of manganese. This method may be followed in the presence of nickel and cobalt.

Method II.—A quantity of bromine water, or 5 or 6 c.c. of bromine, is added to the strongly alkaline solution, with continuous stirring. The liquor is then heated to boiling, when a brownish black precipitate of hydrated manganese peroxide falls. On boiling for a short time, this becomes largely dehydrated, and, on standing, settles.

The liquor is decanted through a filter, the precipitate washed by decantation, and on the filter, dried, transferred to a crucible, ignited, gently at first, afterwards at a high temperature for some minutes, and weighed as Mn_2O_3 , containing 72.05 per cent. of manganese.

It is sometimes recommended to convert the precipitate obtained by bromine into carbonate, but this is unnecessary. If the mineral contain cobalt and nickel they are precipitated by bromine. Any iron left in solution is also thrown down.

In presence of a large quantity of iron the ferric acetate precipitate is liable to carry down manganese, and must be tested by boiling some of the precipitate with nitric acid and lead peroxide. See tests for Mn.

If found, the precipitate must be dissolved in hydrochloric acid, and the precipitation repeated.

* The ore may be ignited to expel organic matter before solution. This, however, generally renders solution more difficult.

† Analysis of cast-iron (p. 351).

VOLUMETRIC METHODS.

These depend on the conversion of the manganese into (a) dioxide, (b) permanganate, the amount of which is estimated by the oxidizing effect it exerts on a solution of ferrous sulphate, or by potassium permanganate.

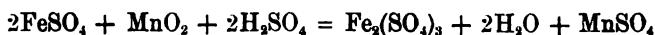
Ferrous Sulphate Method.—For Ores.—Pattinson (iron slags), Kessler (zinc salts). For this purpose the metal is first converted into dioxide, and the precipitate boiled with a known amount of a ferrous salt. Oxidation takes place, and the excess of ferrous salt is estimated by a standard solution of potassium permanganate or bichromate (see p. 177).

One to two grms. of the finely powdered and sifted ore, dried at 100° C., is dissolved in a half-litre beaker in 10–15 c.c. hydrochloric acid with the aid of heat. If the ore does not contain much iron, some ferric chloride or zinc oxide is added, so that there is at least as much iron present as manganese. The solution is neutralized with precipitated granular calcium carbonate* till the liquor becomes reddish. The solution is then diluted with hot water to 300 c.c.; 50–100 c.c. bromine water is then added and heated to 65–70° C. Some further addition of calcium carbonate is made, and the temperature further raised. If any pink colour, due to permanganate, is produced, alcohol is added, drop by drop, till it is discharged by reduction. The precipitate which forms consists of ferric oxide and manganese dioxide. It is filtered through a double paper and thoroughly washed, and added to the ferrous salt.

If it is desired only to estimate the amount of the dioxide in ores, this treatment is unnecessary.

The precipitate is washed into a 300 c.c. flask with boiled water, 10 to 20 grms. of pure ferrous ammonium sulphate (accurately weighed) added, 2 grms. of pure† sodium carbonate, and 50 c.c. of dilute sulphuric acid. The sides of the flask are rinsed down with boiled water, and the precipitate, or ore, mixed by gently rotating the liquid. After a time the flask is gently heated till no black residue remains. The excess of ferrous salt is then estimated by means of standard permanganate of potash or bichromate, as described on p. 177.

The reaction is as follows:—



The excess of ferrous salt found, deducted from the original weight, gives the quantity oxidized.

* This is made by precipitating a somewhat dilute solution of calcium chloride with sodium carbonate, the calcium chloride remaining in excess.

† To generate CO₂ and expel air.

Eighty-seven parts of MnO_2 oxidize exactly 784 parts of ferrous ammonium sulphate containing 112 parts of iron.*

\therefore 1 part MnO_2 oxidizes 9.009 of the salt, or 1.287 grm. (ferrous) iron. or each grm. of the salt oxidized is equivalent to 0.11097 MnO_2 .

Example.—2 grms. of ore were digested as above with 14.859 grms. ferrous ammonium sulphate, and 48 c.c. of permanganate solution with a standard 1 c.c. = 0.0056 were required for the titration.

$0.0056 \times 48 = 0.2688$ grm. iron = 1.8816 ferrous ammonium sulphate.
 $14.859 - 1.8816 = 12.9774$ oxidized.

Since each grm. oxidized is equal = 0.11097, MnO_2

$12.9774 \times 0.11097 = 1.4401$ grm. MnO_2

\therefore weight of sample 2 grms. contains 1.4401 of MnO_2

$$\frac{1.4401}{2} \times 100 = 72.005 \text{ per cent. } \text{MnO}_2$$

Another method of carrying out the test is to dissolve from 1.5 to 2.5 grms. of pure iron wire in sulphuric acid in a 300 c.c. conical flask, using 100–150 c.c. of dilute acid. A Bunsen valve (see p. 173) should be fitted to the flask. When completely dissolved, the precipitate or weighed sample of ore is added, washed down, and digested till dissolved. The residual iron is then estimated as before.

Then, as 1 part MnO_2 oxidizes 1.2873 part of iron (Fe^{II}), each part of iron oxidized = 0.7768 MnO_2 .

The unoxidized iron is deducted from the quantity originally dissolved, and the amount of MnO_2 equivalent to the iron oxidized calculated.

Example.—2 grms. iron were dissolved, and 2 grms. of ore added to the solution. The titration with permanganate took 37.5 c.c. 1 c.c. = 0.01 grm. iron.

$$37.5 \times 0.01 = 0.375 \text{ grm. iron.}$$

$$2 \text{ grms.} - 0.375 = 1.625 = \text{weight of iron oxidized.}$$

$$1.625 \times 0.7768 = 1.2623 \text{ } \text{MnO}_2.$$

$$\frac{\text{MnO}_2 \text{ obtained}}{W} \times 100 = \text{per cent.}$$

$$\therefore \frac{1.2623}{2} \times 100 = 63.115 \text{ per cent. } \text{MnO}_2$$

Estimation of Manganese Dioxide by heating the Ore with an Oxalate and Sulphuric Acid.—(Fresenius and Wills' Method.)—This method, formerly in extensive use, is not now relied on, owing to the uncertainty of the results, as, in the presence of ferrous compounds, it

* As ferrous ammonium sulphate contains $\frac{1}{2}$ of its weight of iron, this factor may be employed in the conversion of one body into terms of the other.

gives the total and not the available MnO_2 , and if carbonates are present the ore requires previous treatment with nitric acid.

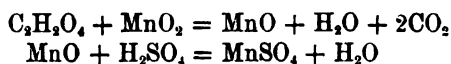
Mohr's Method.—The ore is treated with a known weight of oxalic acid, either in the solid state or in solution, and an excess of dilute sulphuric acid. Heat is applied even to boiling, if necessary, till solution is complete. After cooling, the amount of oxalic acid remaining is determined by means of standard permanganate solution (p. 176).

Any ferrous iron present increases the amount of permanganate used in the titration, and thus diminishes the apparent amount of oxalic acid consumed, in an equivalent proportion, while the presence of carbonates does not interfere. By this treatment an estimate of the manganese oxide available for generating chlorine is obtained, since the ferrous salt would diminish the chlorine liberated in the same proportion as it reduces the oxalic acid consumed.

The standard oxalic acid solution is made by dissolving 63 grms. of the acid in water and diluting to a litre.

The permanganate solution should not be stronger than 5 c.c. permanganate = 1 c.c. of oxalic acid solution. From 2 to 5 grms. of the ore is weighed out, placed in a 300 c.c. flask, and oxalic acid solution, equal to 2 or $2\frac{1}{2}$ times the weight of ore taken, added. Dilute sulphuric acid is added, and heat applied till completely dissolved.

The contents of the flask, after cooling, are titrated with permanganate, the quantity required noted, calculated to oxalic acid, and the amount deducted from that originally used. 90 parts of oxalic acid are equivalent to 87 of MnO_2 ; and



Example.—Weight of ore taken = 3 grms.

Volume of oxalic acid added = 50 c.c. = 3.15 grms.

Volume of permanganate required = 28.5

Standard of permanganate 1 c.c. = 0.01 oxalic acid

Then, $28.5 \times 0.01 = 0.285$

$3.15 - 0.285 = 2.865$ grms. consumed

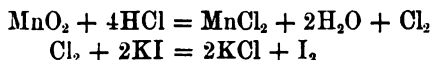
$\therefore \frac{2.865}{90} \times 87 = 2.7693$ grms. MnO_2

and $\frac{2.7693}{3} \times 100 = 92.31$ per cent. MnO_2

This method involves one weighing only.

Estimation of Manganese Dioxide by the amount of Iodine liberated from Potassium Iodide, when treated with Hydrochloric Acid (Bunsen's Method).—In this method of estimation the ore is heated

with strong hydrochloric acid, and the chlorine liberated led into a strong solution of potassium iodide, whereby iodine is set free. The amount liberated is determined by means of standard sodium thio-sulphate solution and starch.



Thus, $\text{I}_2 = \text{MnO}_2$, or 254 parts of iodine are liberated for each 87 of MnO_2 in the ore.

This method, being unaffected by any impurities in the ore, gives accurate results of the chlorine generating power of the substance.

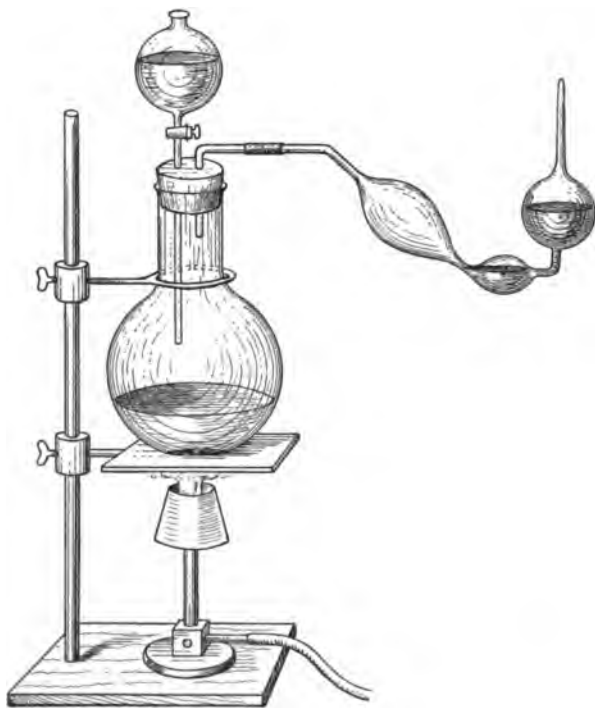


FIG. 77.

Careful manipulation is, however, necessary. The apparatus shown in Fig. 77 may be used. The flask is fitted with a rubber cork (previously boiled in dilute caustic soda to remove sulphur) and leading tube, and, for simplicity, nitrogen bulbs are shown as containing the absorbent.

Fig. 78 shows a very efficient absorbing arrangement. The beaker contains a funnel with an indented edge, through the stem of which passes a bulb tube, extending nearly to the bottom. The tube fits the funnel stem, and is attached by a piece of rubber tube previously boiled in soda, which passes over the funnel stem and tube.

The bulbs or other apparatus for absorption are filled with a concentrated solution of potassium iodide, suitably supported, and placed in a vessel containing cold water.

The weighed sample is placed in the flask, the cork replaced, and a considerable excess of hydrochloric acid added from the funnel.

After the lapse of a short time heat may be applied—gentle at first and gradually increased to boiling. The liberated chlorine, together with hydrochloric acid gas, passes over and is absorbed by the iodide solution, which becomes brown by dissolving the liberated iodine.

The boiling is continued till decomposition of the ore is complete, and the chlorine has been completely swept into the iodide solution by the steam and hydrochloric acid. This may be recognized by holding a white sheet of paper behind the flask. Care must be taken by regulating the heat to prevent the iodide solution rushing back into the flask. It is better to employ a flask having a cork with three holes, and lead a gentle stream of carbon dioxide through the apparatus while dissolving, but with care this is unnecessary.

When decomposition is complete, the bulbs are detached before removing the burner or stopping the carbon dioxide, the solution transferred to a beaker, and the bulbs washed out. Any large excess of acid may be partially neutralized with very dilute ammonia, taking care to leave the solution distinctly acid. [For obvious reasons it will not do to add excess of ammonia, and then acidify.] If any free iodine is seen floating about as brown flakes or scum, some solid potassium iodide is added to dissolve it.

The solution is then cooled and titrated with standard sodium thiosulphate (hypo). When the colour becomes lighter, starch solution is added, and the titration continued till the blue colour disappears. The sensitiveness of the reaction causes the end to be very sharply defined, and near the end the solution must be added drop by drop (see p. 85).



FIG. 78.

The standard solution of thiosulphate used contains 25 grms. to the litre.

1 c.c. = 0.0127 gm. iodine = 0.00435 MnO_2 . It must be standardized.

The starch solution is made as directed on p. 86.

Standardizing.—This may be effected with pure re-sublimed iodine, 0.5 gm. being dissolved in twice its weight of potassium iodide, diluted to 150 c.c., and titrated. The value of each c.c. of the thiosulphate solution is calculated in terms of iodine, chlorine, and manganese dioxide, and marked on the bottle.

Example.—

Weight of ore taken	= 0.5 gm.
Weight of KI in bulbs	= 6 grms.
Volume of sodium thiosulphate used			= 99.8 c.c.
1 c.c. solution in terms of MnO_2			= 0.00435 gm.
Quantity of MnO_2	= 99.8×0.00435
			= 0.43413
Percentage in ore	= $\frac{0.43413}{0.5} \times 100$
			= 86.826 per cent.

Pure copper may also be used for standardizing.

The thiosulphate solution must be re-standardized every few days.

The assay solution must be titrated without delay, as the hydriodic acid liberated by the hydrochloric acid decomposes on standing, and the results obtained are too high. If delayed a few hours the error may amount to 3 or 4 per cent.

This method of estimation is not interfered with by any of the common impurities,—oxides or carbonates,—and gives the chlorine generating power of the ore.

Estimation of Manganese by precipitation with Potassium Permanganate (Gruyard and Volhard's Processes).—Potassium permanganate added to solutions of manganous salts precipitates the manganese as manganese permanganate in reddish-brown flakes, or in presence of zinc salts as a flocculent precipitate of MnO_2 . Any excess of permanganate is made apparent by its pink colour, while iron and other bodies which would reduce permanganate can be peroxidized without interfering with the manganese.

One or two grms. of the substance to be assayed is dissolved in aqua regia. The solution is boiled for some time to completely expel chlorine, and nearly neutralized. It is then diluted to 200 c.c. with boiling water (or boiled if sufficiently bulky), and titrated slowly with potassium permanganate solution at a temperature not below 80°C ., but not boiling. The manganese precipitate subsides quickly, but, should it

not, settling may be hastened by warming (not boiling). When a permanent rose tint is acquired after shaking, the titration is finished.

A. Gruyard uses pure manganese sulphate, dried at a high temperature, for standardizing. Ferric and chromic compounds, if in large quantity, interfere with the reactions.

Estimation of Manganese by Standard Potassium Permanganate Solution (Volhard's Process), specially applicable to iron containing manganese.—From $\frac{1}{2}$ to 1 grm. of the spiegel or ferro-manganese is weighed out, and dissolved in the minimum amount of nitric acid, 1.2 sp. gr.; 25 c.c. is sufficient for 1 grm. When action is complete, 12 c.c. of dilute sulphuric acid (1 : 1) is added, and the liquid carefully evaporated till sulphuric acid fumes are given off. Nitric acid is thus expelled. After cooling, the liquid is diluted to about 500 c.c., and carefully neutralized with sodium carbonate. It should be just neutral, or faintly acid. Zinc oxide suspended in water is then added in slight excess. As soon as the zinc oxide is in excess, the precipitated ferric oxide coagulates on settling. The liquid is heated to boiling, and, while hot, the standard permanganate is added from a burette.

After each addition, the precipitate is allowed to settle, and the addition of permanganate continued till a faint rose tint which remains, after shaking, and standing for a minute, is obtained in the liquid. The manganese is precipitated as manganate of manganese.

It is best to add nearly the whole of the permanganate required at once, within a c.c. or so. In examining unknown alloys, or ores, some preliminary assays should be made to determine the amount necessary. Or, after adding the zinc oxide, the sample is diluted, to say 500 c.c., and the temperature of the liquid taken. Filter off—through a dry paper—some 400 or more c.c. of the solution. Heat to the temperature of dilution, and measure out 100 c.c. = $\frac{1}{5}$ of original weight, boil and titrate. Repeat carefully with other portions.

COLORIMETRIC MANGANESE DETERMINATION.

For this purpose the manganese is converted into either manganate or permanganate.

Manganate Method.—0.1 grm. of a substance, containing a known quantity of manganese, is put into a deep porcelain crucible, capable of holding 30 c.c., and treated with 2 c.c. strong HNO_3 . The solution is evaporated to dryness, and the residue heated till completely decomposed. It is broken up, heated with 2 c.c. concentrated caustic potash solution, evaporated to dryness without spirting, and fused gently. After cooling,

the residue is dissolved in water, and made up to 25 c.c. Five c.c. of this solution is transferred by a pipette to a graduated test-tube (Eggertz tube), and is employed as the standard.

The sample is treated in the same manner, and under the same conditions. Any precipitate that remains on dissolving the mass after fusion with potash is allowed to settle before taking the 5 c.c. for comparison. The solution which has the deeper tint is then diluted till both have the same depth of colour. Since the same weights of substance are taken in each case, the manganese present is proportional to the volume. Thus—

0.1 standard, containing 0.75 per cent. Mn.

Dilute to 25. 5 c.c. taken.

Final volume, 5 c.c.

0.1 substance.

Diluted to 25 c.c. 5 c.c. taken.

Final volume, 5.4 c.c.

$5 : 5.4 :: 0.75 : \text{per cent. Mn} = 0.81 \text{ per cent.}$

Permanganate Method.—The sample, which must be free from chlorine, is boiled with nitric and sulphuric acid, and peroxide of lead (or red lead), whereby any manganese present is oxidized to permanganic acid.

A sample, containing not more than 50 mg. of Mn, is dissolved by boiling in a mixture of nitric and sulphuric acids, containing 20 c.c. nitric and 5 c.c. sulphuric acid per 100 c.c. From 20–25 c.c. of this mixture is used, or more if necessary, and 2 or 3 grms. of peroxide of lead added. After solution, the liquid is allowed to settle, filtered through asbestos, and the residue washed by decantation, with very dilute sulphuric acid. The solution is made up to a known volume, dependent on the depth of colour, 5 c.c. taken, and compared with a standard made of 0.1435 gm. of potassium permanganate, dissolved in a litre of water. 1 c.c. = 0.00005 gm. of Mn.

Example.—5 grms. of steel was dissolved diluted to a litre, and 5 c.c. taken for comparison.

5 c.c. of the standard had to be diluted to 5.6 c.c.

1 litre of the standard solution contains 0.05 gm. Mn.

1 „ „ steel „ „ $5.6 : 5 :: 0.05 (0.00005 \times 1000) = 0.04464.$

Thus 5 grms. : 100 grms. $:: 0.04464 = 0.892 \text{ per cent. Mn.}$

CHROMIUM.

THE identification and estimation of this metal are required in the following bodies :—

Chrome iron ore.

Chromic oxide (chrome green).

Chromates and dichromates.

Ferro-chrome.

Chrome-steel.

Slags.

Chrome Iron Ore.—**Chromite** (FeOMgO), Cr_2O_3 .—The crystals are regular octahedra, but the mineral generally occurs massive and granular, associated with serpentine and granular limestone. Lustre, dull to metallic. Fracture, uneven. Colour, brownish to iron black. Streak, reddish brown. Sp. gr., 4.0–4.5. Hardness, 5.5. Magnetic after heating in reducing flame, if not before. Usually contains from 30–60 per cent. of Cr_2O_3 .

Chrome Ochre is a dull green, or yellowish green oxide, occurring with chrome iron ; distinguished from nickel oxide by being soluble in potash.

Chrome Green is the anhydrous oxide, Cr_2O_3 .

Chromates and **dichromates** are yellow and red salts. Those of the alkalis are soluble, those of lead and other metals are insoluble. Crocoisite—a naturally occurring red chromate of lead—and vanquelinite—a chromate of lead and copper—occur native in small quantities.

Ferro-chrome is a silvery white, crystalline, hard alloy of iron and chromium and other elements, used for the addition of chromium to iron in the manufacture of chrome steel, and may contain 65 per cent. or upwards of metallic chromium. It does not tarnish.

Slags from chrome steel making, and the manufacture of ferro-chrome, often contain chromium.

REACTIONS FOR CHROMIUM.

Dry Tests.—On charcoal in the reducing flame chromium compounds yield a mass which, in the case of chromite, is magnetic.

If a little of the finely powdered substance be mixed with sodium carbonate and potassium nitrate and heated on platinum foil, any chromium present is converted into potassium chromate, and a yellow mass results. If this be dissolved in water, the solution acidified with acetic acid, and lead acetate added, a yellow precipitate falls.

In borax bead chromium gives a green colour, which is unaltered in the reducing flame.

Chromic salts are green in colour. Chrome alum, isomorphous with ordinary alum, is violet; chromic acid, red; chromates, yellow, and bichromates, red.

Wet Tests.—Solution containing chromium salts behave as follows :—

Hydrochloric acid and sulphuretted hydrogen yield no precipitates; the chloride being soluble, and the sulphide soluble in acids.

Ammonia precipitates a pale greyish-green precipitate of chromic hydrate, $\text{Cr}_2(\text{HO})_6$, slightly soluble in the cold, but completely precipitated on boiling. Tartaric acid and other organic substances prevent this precipitation.

Sodium hydrate produces the same precipitate, which dissolves completely in excess in the cold, but is precipitated by long boiling or the addition of ammonium chloride.

Ammonium chloride in large excess completely precipitates the hydrate from neutral solutions.

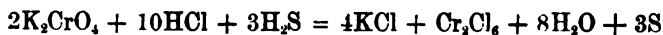
Barium carbonate in neutral solution precipitates the chromium as a basic salt.

Ammonium sulphide precipitates the hydrate. This is due to the decomposition of the sulphide by water.

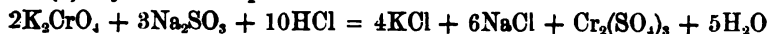
Chromic Acid and Chromates.—Treatment of chromic salts with oxidizing agents in the presence of bases, as, for instance, boiling with nitric acid and potassium chlorate, converts chromium and its compounds into chromates which dissolve to a yellow solution, with which after neutralization—

1. Lead acetate gives a yellow precipitate of lead chromate, PbCrO_4 .
2. Barium chloride precipitates pale yellow barium chromate, BaCrO_4 .
3. Silver nitrate throws down red silver chromate, Ag_2CrO_4 .

Chromates are readily reduced to chromic salts in acid solution by ordinary reducing agents, *e.g.* (a) by sulphuretted hydrogen.



(b) By sodium sulphite.



(c) Or, by adding a little sulphuric acid, then alcohol, and warming.

In each case the solution changes from yellow to green, owing to the formation of the chromic salt.

ESTIMATION OF CHROMIUM.

Determination of Chromium in Chrome Iron Ore.—Chrome iron ore is exceedingly difficult to dissolve. It must first be finely ground, finishing in an agate mortar, and finally sifted through gauze or muslin. A convenient way is to tie the muslin over the top of a dry beaker, put the ground material on the top, and then tie over it a piece of thin sheet rubber. By drumming on the rubber with a small spatula the powder is passed rapidly through.

The methods of solution are:—

Fusion with Potassium Bisulphate (Genth's Method).—0.5 gm. of the ore is fused with 6 grms. of the salt at a gradually increasing temperature for 20 minutes, 3 grms. of pure sodium carbonate added, and the fusion continued for another hour, adding by degrees 3 grms. of potassium nitrate. Finally the fusion is maintained at full redness for fifteen minutes. The fused mass is boiled with water, filtered hot, and washed. Any undecomposed black residue must be re-treated.

The solution is evaporated nearly to dryness with excess of ammonium nitrate till ammonia is expelled, and the precipitated silica, manganic oxide, etc., filtered off. The chromium remains in solution as chromic acid. This is reduced by adding a large excess of sulphurous acid, and boiling, and the chromium estimated gravimetrically.

Fusion with Sodium Hydrate and Sodium Peroxide.—6–10 grms. of caustic soda are placed in a silver crucible and melted to quiet fusion, 0.5 gm. of the ore added as uniformly as possible and stirred with a silver wire. The dish is heated to incipient redness, and about 3 grms. of sodium peroxide is added in small quantities at a time, stirring after each addition, and the heating continued till oxidation is complete. The residue is extracted with hot water, and the chromium estimated gravimetrically or volumetrically. See below.

Heating with Lime and Sodium Carbonate (Kayser's Method).—The finely powdered mineral is heated with about 10 times its weight of a mixture of 2 parts sodium carbonate and 1 part pure lime. This is placed in an open crucible or dish, and heated at bright redness in a muffle, with frequent stirring for from half an hour to an hour. The

chromate formed is extracted with water, and the chromium estimated either volumetrically or gravimetrically.

Fusion with Sodium Hydrate and Magnesia (Clarke's Process).—Two grms. of finely powdered ore are intimately mixed with 10 grms. of sodium hydrate and 6 grms. of magnesia, and heated in a platinum crucible, with the lid on, for three-quarters of an hour to an hour at bright redness. At first the flame should be as low as possible, the intensity being gradually increased, so that at the end of a quarter of an hour the gas is full on. The crucible and contents are treated with water, in a porcelain basin, and the solution hastened by the addition of a little pure sulphuric acid. When solution is complete (except perhaps a little silica), the crucible is washed and removed, the solution acidified, and the chromium estimated volumetrically.

Fusion with potassium bisulphate and sodium fluoride is sometimes resorted to for the solution of chrome iron.

Britton's Method.—The solution of the chromium is effected by fusion with 8 times its weight of a mixture of potassium chlorate and soda lime, 1 part of the former to 3 of the latter. The ignition is continued for an hour and a half at bright redness. After solution in hydrochloric acid, the chromic acid present is estimated volumetrically.

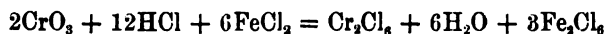
Gravimetric Estimation as Cr_2O_3 .—The solution* is boiled for some time to completely precipitate iron, the liquid slightly acidified with nitric acid, and ammonia added in slight excess to precipitate alumina. This is washed by decantation. The liquor containing the chromium as chromate is reduced by sulphurous acid and evaporated to dryness to separate silica. It is then taken up with dilute hydrochloric acid, silica filtered off and washed, and ammonia added in excess, the solution boiled vigorously for a few minutes, and the precipitate filtered off and washed by decantation and on the filter. It is better to wash it back again into the beaker, boil with water, and re-filter, in order to get it free from sulphates and alkaline salts. The precipitate is then dried, ignited, and weighed as Cr_2O_3 . If alkalies remain in the precipitate, they will, during ignition, form chromates, and it becomes necessary to treat the precipitate with water, reduce with sulphurous acid, re-precipitate with ammonia, filter, wash, etc., in order to obtain the oxide pure. Factor for Cr = 0.6864.

Volumetric Estimation.—The solution containing the chromium as a soluble chromate is acidified, heated to boiling, and a known quantity of ferrous ammonium sulphate — 16 to 20 grms. carefully weighed — or a solution of ferrous iron (see Manganese), is added. The ferrous salt added must be more than sufficient to completely

* If not already alkaline, caustic soda must be added in excess.

decompose the chromate. The excess of ferrous iron is then estimated by titration with a weak solution of potassium dichromate (see Iron).

The amount of iron found by titration deducted from the total quantity added gives that oxidized by the chromic acid formed in the fusion, and as



336 parts of iron (as FeCl_2) are oxidized by 104.2 of Cr as CrO_3 ,

$$\frac{104.2}{336} = 0.31 \text{ parts of chromium, or } 0.4522 \text{ grm. of } \text{Cr}_2\text{O}_3.$$

\therefore weight of iron oxidized $\times 0.31 = \text{Cr}$.

and „ „ „ $\times 0.4522 = \text{Cr}_2\text{O}_3$.

Estimation of Chromium in Chrome Iron and Steel.—The alloy is dissolved in sulphuric acid with the aid of heat, and the iron peroxidized by the addition of nitric acid. The liquor is then evaporated till fumes of sulphuric acid are evolved and all free nitric acid is expelled. If manganese is absent, sulphate of manganese, equal in quantity to the chromium present, is added. The chromium in solution is then oxidized to chromate by the careful addition of potassium permanganate to the hot solution until a pink colour is obtained. The solution is then boiled till the pink colour is destroyed and a precipitate forms. If no precipitate forms, two or three drops of permanganate should be added and the solution boiled, but perfect discoloration must take place. The excess of permanganate is precipitated by the manganese present (see Manganese.) To the solution thus prepared a weighed quantity of ferrous ammonium sulphate, or a solution containing a known weight of a ferrous salt, is added, and the excess of ferrous iron estimated by bichromate as before.

TITANIUM.

THIS metal has usually to be determined in the following bodies :—

Rutile. Anatase. Brookite, TiO_2 .

Titanate of lime, CaOTiO_2 .

Sphene. Titanosilicate of lime, $\text{CaO}, \text{TiO}_2, \text{SiO}_2$.

Ilmenite and titaniferous iron ore.

Also in clays, bauxite, clay iron-stones, stream tin, and in certain granites, basalts, dolerites, and other igneous rocks.

A copper-red crystalline body of extreme hardness occurs in the “bear” of blast furnaces, and is a cyano-nitride of titanium.

Certain irons smelted from titanic ores occasionally contain very small quantities of the element, which, although regarded as one of the rarer elements, is widely distributed in small quantities.

Slags from such ores contain the bulk of the titanium present.

Rutile is isomorphous with tin-stone. It crystallizes in the tetragonal system in octahedra, often with basal planes, and also occurs massive. Colour, from dark ruby to steel grey or black. Thin flakes are red. Streak, yellowish brown. Lustre, adamantine to metallic. Hardness, 6·5. Brittle. Sp. gr., 4·2–4·3. Blow-pipe reaction (see below).

Brookite is rhombic (monoclinic, Schrauf), in six-sided crystals. Lustre as rutile. Colour, yellow, red, or hair brown. Streak, whitish.

Anatase is tetragonal, in pyramidal crystals with basal planes. Colour varies. Sp. gr., 3·8–3·93. Hardness, 5·5–6.

Sphene. The silico-titanate of lime is monoclinic. Colour, brown, yellow, or greenish. Lustre, resinous to adamantine. Hardness, 5–5·5. Sp. gr., 3·4–3·6.

Titaniferous Iron Ore occurs in crystals belonging to the hexagonal system, massive, and in grains. Colour, iron black to steel grey. Lustre, dull to submetallic; opaque. Streak, black to brownish. Only very slightly magnetic. Hardness, 5–6. Sp. gr., 4·6–5. It is a double oxide of iron and oxide of titanium.

REACTIONS FOR TITANIUM.

Dry Tests.—Titanic oxide is infusible before the blow-pipe. Ilmenite is also infusible. Sphene melts on thin edges to a black glass.

With microcosmic salt in the oxidizing flame titanic oxide gives a bead, which in the reducing flame becomes yellow while hot, and violet when cold. This change is best obtained by the addition of tin. If an iron salt is present, or be added to the bead, it becomes almost blood-red on heating.

Wet Tests.—Native titanic oxide, like cassiterite and silica, is insoluble in hydrochloric and nitric acids. The titanates are somewhat soluble. In solutions containing titanium salts—

Sulphuretted hydrogen produces no precipitate.

Ammonia produces a white precipitate of titanic hydrate, insoluble in excess or in ammonium carbonate, if boiled, but soluble in acids.

Hydrofluoric acid in strong solution of potassium titanate deposits on standing a white precipitate of potassium fluotitanate, in scaly crystals. To obtain this the substance tested must be fused with potassium carbonate, and the solution obtained by boiling with water, neutralized with hydrofluoric acid.

Solutions containing titanic acid, when treated with zinc and hydrochloric acid, give a blue or violet colour, owing to the reduction of the titanic oxide to sesquioxide yielding Ti_2Cl_3 .

Titanic oxide is precipitated from its acid solutions by long-continued boiling.

Alkalies and ammonium sulphide do not precipitate titanium in presence of tartaric acid.

Hydrogen peroxide added to acidified solutions of titanium produces a yellow to dark brown coloration. Nitric acid solutions of ammonium molybdate give the same colour, but molybdenum must be distinguished by the spectroscope.

The solution in carbonated alkalies is precipitated by boiling with ammonium chloride.

ESTIMATION OF TITANIUM.

The oxide usually occurs in the undissolved residue remaining from the ordinary treatment with acids; but if titanates were present, some will be found in the acid solution.

The ore or mineral to be examined for titanium is treated with acids

in the usual way, evaporated to dryness, taken up with hydrochloric acid, and filtered.

(a) The residue. This is moistened with sulphuric acid, hydrofluoric acid added, and carefully evaporated to dryness. This treatment is repeated once or twice to remove silica as volatile silicon fluoride. The residue is dried, mixed with bisulphate of potash, and fused, preferably in a platinum vessel. The fused mass is allowed to cool, and extracted repeatedly with cold water. The residue contains some of the rarer earths and unremoved silica. The solution is largely diluted, acid-sulphate of soda added, and boiled for some considerable time to precipitate the titanic oxide. When precipitation is complete, a little sulphurous acid is added to dissolve any iron or alumina, and the precipitate is filtered and washed.

(b) The solution. After removing the metals of Group II. by saturating with sulphuretted hydrogen the iron is peroxidized by nitric acid, the solution carefully neutralized, and members of the iron group, etc., removed by means of sodium acetate as basic acetates (see p. 200). This precipitate, which contains the titanium, is collected, dried, mixed with six times its weight of potassium bisulphate, and fused. The mass is extracted with cold water, filtered, diluted, very slightly acidified with sulphuric acid, and the titanic acid precipitated by prolonged boiling, as before, and filtered.

The precipitated titanic acid may be dried, ignited with a little ammonium carbonate, and weighed as TiO_2 , or it is converted into potassium fluotitanate by mixing the dried precipitate with potassium carbonate in excess and fusing. The resulting mass is dissolved in water and the solution neutralized with hydrofluoric acid, and set aside. The fluotitanate, $K_2TiF_6 + H_2O$, which separates is collected in a filter, washed with a few drops of cold water, dried in an air bath, and weighed, as K_2TiF_6 .

The oxide, TiO_2 , contains 60·98 per cent. of titanium, and the titanofluoride of potassium after heating contains 19·98 per cent.

TUNGSTEN

Occurs principally as wolfram (tungstate of iron and manganese), scheelite (tungstate of lime), and to a less extent as tungstic acid (WO_3).

It is met with as an addition to steel (self-hardening), and in the form of tungstic acid and tungstates used for mordanting purposes.

Wolfram crystallizes in the monoclinic system, but is most often met with as a heavy iron-black mineral, with distinct cleavage. Colour,

iron-black. Lustre on cleavage, metallic to adamantine. Streak, black-brown. Hardness, 5-5.5. Sp. gr., 7-7.5.

Scheelite.— CaWO_4 , is tetragonal; occurs also massive. Colourless, grey, yellow, or brown. Streak, white. Hardness, 4-4.5. Sp. gr., 5.9-6.2.

Tungstic ochre is a brownish pulverulent or earthy body.

Tungsten steel is self-hardening, and exhibits a very close fracture tinged with brown.

REACTIONS FOR TUNGSTEN.

Dry Tests.—Wolfram, before the blow-pipe, fuses to a black magnetic globule. Scheelite yields a translucent glass.

With microcosmic salt and tin tungsten compounds yield in the reducing flame a dirty green bead while hot, and a blue bead when cold. If iron is present, the bead is bluish red.

Substances containing tungsten are converted into tungstates by fusion with caustic alkalies and nitre.

Wet Tests.—The salts of tungsten are rarely met with commercially. Most of them are decomposed by water yielding brown residues.

The Tungstates.—

(1) Hydrochloric acid precipitates yellow tungstic acid insoluble in excess or in alcohol, but soluble in ammonia. Fusion of the precipitate with caustic potash or soda converts it into a tungstate, which is soluble in water.

(2) Solutions of tungstates, on the addition of zinc and hydrochloric acid or stannous chloride, become blue owing to the reduction of the tungstic acid.

(3) If ammonium sulphide be added and then dilute hydrochloric acid, a brown precipitate of tungsten sulphide falls.

(4) In the treatment of minerals with acids, tungstic acid is left as a yellowish brown residue mixed with the other insoluble matter.

Estimation of Tungsten in Wolfram.—Two grammes of the very finely divided mineral (sifted through muslin) are digested with 25 c.c. a mixture of four parts hydrochloric acid and one part nitric, at a gentle heat, till action ceases, and the solution evaporated to dryness. Water is added, and the solution warmed till the chlorides of iron and manganese are dissolved. The residue consists of tungstic acid, silica, niobic acid, tantallic acid, and possibly titanlic acid. Wash as completely as possible by decantation through a filter. Cover the residue in the dish or beaker with ammonia (1 : 1), and wash back any residue on the filter into the dish and stand aside in a warm place. Decant the liquid as completely

as possible (through a filter) into an evaporating dish, and wash the residue also by decantation. If the residue is black, treat it with a further quantity of hydrochloric and nitric acids, and repeat the treatment with ammonia, as before, till a white residue only remains.

The ammoniacal solution of tungstate is cautiously evaporated to dryness, and gently heated to decompose the ammonium tungstate. Yellow tungstic acid remains, and, after the decomposition is complete, may be strongly heated, and weighed when cool. It contains 79.31 per cent. of tungsten.

The precipitate may be tested for silica by fusing it with acid potassium sulphate and extracting with water and dilute ammonium carbonate. Silica remains undissolved, and its weight must be deducted.

If the oxide is reduced while heating, by gases getting into the crucible, the residue will be greenish.

The residue left, after treating the mineral with acid, often contains about 2-2.5 per cent. of niobic and tantallic oxides.

Tungstic acid in tungstates may be estimated by evaporation to dryness with hydrochloric acid extraction with water, solution of the tungstic oxide in ammonia, and treating as above.

Tungsten in steel (see p. 367).

TIN.

SUBSTANCES in which the metal has to be determined—

- (a) Ores.
- (b) Mattes.
- (c) Slags.
- (d) Alloys and metallic matters, *e.g.* "hardhead," etc.

Ores.—**Tinstone, Cassiterite, Stream and Wood Tin, Stannic Oxide** (SnO_2). Crystallizes in tetragonal forms, often twinned. It has a brilliant adamantine lustre, is not scratched by knife (hardness, 7), heavy (sp. gr., 6.4–7.1). The colour varies from yellowish to black. It occurs generally in granitic and micaceous rocks, and in certain alluvial deposits, as stream tin. It contains 78.38 per cent. of tin when pure, but ores often contain only 1 or 2 per cent. of tinstone. Heated on charcoal with a mixture of sodium carbonate and potassium cyanide, a bead of tin results.

Stannine, Tin Pyrites, Bell Metal Ore, $2(\text{Cu}_2\text{FeZn})\text{S}, \text{SnS}_2$.—Contains copper, iron, zinc, and tin as sulphides. It has an iron black or bronze colour, with a purplish tarnish, but is often yellow from excess of copper pyrites. It is scratched by a knife (hardness, 4), sp. gr. about 4.5. It usually contains about 27 per cent. of tin, but the composition varies greatly. Fuses on charcoal when heated.

Black Tin is the tinstone after calcining, lixiviating, and washing to remove arsenic, copper, iron, and sulphur.

Mattes occasionally contain tin in considerable quantity.

Slags.—Slags from tin smelting, especially in blast furnaces, frequently contain the oxide and shots of metal, giving a whitish and spotted, filmy, or opalescent appearance, as silicate.

Alloys.—**Bronze, Gun-metal, and Engineer's Brass** are alloys of copper and tin with variable amounts of other metals.

Solders.—**Tinman's solder, plumber's metal, etc.**, are alloys of lead and tin. Stereotype metal, Britannia metal, and pewter contain tin, lead, and antimony.

Bearing Alloys.—Many white bearing alloys consist of tin, lead, antimony, and copper.

Pattern alloys consist of tin and zinc.

Phosphor Tin is a phosphide of tin of variable composition. It generally contains from 2 to 11 per cent. of phosphorus.

REACTIONS OF TIN.

Tin dissolves readily in hydrochloric acid, and with less ease in sulphuric acid. When heated with strong nitric acid it is converted into metastannic acid. Treated with weak nitric acid it is dissolved, but is precipitated on boiling as H_2SnO_3 , which is insoluble in nitric acid, and remains as a white powder. When heated, the H_2SnO_3 loses water, and leaves stannic oxide, SnO_2 . The metal, when heated, oxidizes readily, ultimately forming SnO_2 . At a white heat it volatilizes more or less freely.

Tin oxide, artificially obtained, unless strongly ignited, is soluble in hydrochloric and sulphuric acids. The native oxide is not attacked by acids, but is rendered soluble by fusion with caustic potash, which produces soluble potassium stannate.

Dry Reactions.—Mixed with sodium carbonate and potassium cyanide, and heated on charcoal in the blowpipe flame, tin compounds yield a soft malleable metallic bead.

Wet Reactions.—Hydrochloric acid produces no precipitate, the chlorides being soluble.

Sulphuretted hydrogen gives with stannous salts a brown precipitate, and with stannic salts a yellow precipitate. Both are insoluble in dilute hydrochloric acid, but dissolve readily in caustic soda and sodium and ammonium sulphides, and in hot concentrated hydrochloric acid. The sulphides are converted into SnO_2 by roasting, or by treatment with strong nitric acid.

Ammonia produces a gelatinous precipitate, which, however, becomes granular on boiling with strong sodium sulphate solution, and is readily filtered.

Caustic soda produces the same precipitate, but soluble in excess.

Mercuric chloride in a solution of stannous chloride gives a white precipitate of calomel, Hg_2Cl_2 , which, in presence of excess of stannous chloride, turns grey on warming, being reduced to metallic mercury.

Gold chloride in partly oxidized stannous solutions gives a purple precipitate (purple of cassius).

Zinc precipitates metallic tin from both stannic and stannous solutions.

In examining ores for tin, the finely powdered material should be

first very carefully washed, on a vanning shovel (Fig. 79) or pan, to separate earthy matters. The residue should then be roasted, to expel sulphur, arsenic, etc., and again washed, to remove oxides of iron, copper, etc., produced by the roasting. The residue should be dried and tested on charcoal before the blowpipe, or boiled with dilute hydrochloric acid and filtered, the insoluble residue fused with potassium cyanide, dissolved in nitro-hydrochloric acid, the solution boiled with copper for some time in strongly acid solution, and mercuric chloride added. A white or grey precipitate indicates tin.

The detection of tin in alloys is effected by dissolving the alloy in strong nitric acid, when the metal is converted into metastannic acid, and remains as an insoluble white powder. This is filtered off, and, to distinguish from antimony oxide, which would also remain, is dried, heated with ammonium nitrate till the excess of the salt has been volatilized, the residue boiled repeatedly with tartaric acid till sulphuretted hydrogen no longer produces a precipitate in the solution, and the residue fused with potassium cyanide. If tin oxide be present, globules of tin are obtained.

Or, the residue from nitric acid may be dissolved in hydrochloric acid, and a piece of platinum foil and a rod of pure zinc introduced into the solution, the two metals being brought into contact outside the liquor. If the white residue be oxide of antimony, the metal is deposited as a grey film on the platinum; but if oxide of tin, as a spongy mass on the zinc, or perhaps as floating flocks of metallic tin. This must be removed, dissolved in hydrochloric acid, and the solution tested with mercuric chloride or sulphuretted hydrogen.

VANNING ASSAY OF TINSTONE.

The high specific gravity of tinstone (7.1), as compared with its common earthy associates, felspar, quartz, schorl, spinel, chlorite, etc., etc., together with its unalterability on heating, permit of a rough assay of the lode stuff being made by washing the finely crushed material, to remove light earthy matters, calcining the residue, to convert heavy metallic minerals, such as copper and iron pyrites, and mispickel into oxides (and to remove sulphur and arsenic), and again washing. The oxides, being light, are thus removed. The residue is weighed.

The Operations are conducted as follows :—A weighed quantity of the finely powdered and carefully sampled mineral is taken.

A full test weighs about 25 grms. (special weights are employed at the mines), but for rich ores, half or a quarter of this amount will be sufficient.

The sample is placed in the centre of the vanning shovel, Fig. 79 (a sheet-iron dish, 14 by 13 ins., with a light handle about 3 ft. long), weighing about 2½ lbs. The washing is conducted in a kieve (4 ft. long by 2 ft. 6 ins. wide), or tub of water. The vanner places the shovel on the top of the water, and by lowering the edge allows about 50 c.c. of water to flow on to the

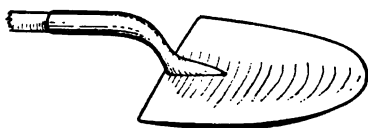


FIG. 79.

shovel. The edge of the shovel is then raised, and by a rapid circular or elliptical motion the water is agitated with the ore.

The lighter particles remain suspended in the water, which after a momentary rest is poured off. This is repeated till the water ceases to be muddy. To remove the larger particles of foreign matter, the vanner takes a less quantity of water, and washes with a circular or slightly elliptical motion, and just as the water-wave reaches the front gives the shovel a slight jerk forwards. This throws the heavy stuff up towards the front, and the water brings the lighter material back, so that it can gradually be washed off. The residue corresponds to dressed tin ore. It is dried on the shovel, and calcined either in a crucible in the wind furnace, or better on a roasting-dish in a muffle.

The residue after calcining is again placed on the shovel, rubbed down with a hammer, and washed as at first. The final washing must be very carefully conducted.

The heaviest portions, after separation (jerking motion), are left high up on the shovel to leave room for the more careful washing of the lighter part. The quantity of water used is about 15 to 20 c.c. at a time, and the movement of the particles under the water is a guide as to their character. The heavier ones gradually work back towards the "crop." The tailings are again rubbed down, and the washing continued till no more tin is thrown up. Somewhat vigorous agitation is required to throw up the last portions of the finely divided ore. The tailings are then washed off, and the whole crop is finally washed once or twice with a little water, and dried. Any particles of iron or magnetic iron ore are removed by a magnet, and the residue weighed. It corresponds to the black tin of the smelter, and averages about 92.5 per cent. of tin oxide. The amount of tin is calculated on this assumption.

At the Cornish mines a standard weight of 200 is employed, representing a ton divided into 200 parts; so that every 10 parts of tin-stone obtained is equivalent to 1 cwt. per ton. The valuation of a parcel is therefore easily accomplished.

This process is at best only a miner's rough method. Wolfram is not separated, and the tinstone is not pure. Good results are nevertheless obtained by careful manipulation. The produce may be afterwards assayed, and the percentage of tin it contains found.

DRY ASSAY OF TIN.

These methods are generally adopted for the assay of tinstone, black tin, stream tin, etc. The ore, if necessary, must be vanned before assay.

Fusion with Anthracite (Cornish Method).—In this assay the black tin is simply heated with anthracite culm in a black-lead crucible. The ore is finely powdered, and sifted through an 80 sieve, 40 to 80 grms. of ore is taken (20 grms. is quite sufficient, if of good quality), and mixed with one-fifth of its weight of finely powdered anthracite.

The mixture is put into a black-lead crucible, and heated to whiteness for 20 minutes. The sides of the pot are scraped down with an iron rod or charred stick, and the heating continued a few minutes longer. When the pot is removed from the fire, it is tapped or shaken gently, to make the globules of tin coalesce. The contents of the crucible are poured into an iron mould, placed on a tray to receive the residue of anthracite and slag (culm ash) that remain—and which fall over the mould. The pot is carefully scraped out. After cooling, the tin button is removed, and the powdery residue transferred to a mortar and ground. The powder is sifted to remove any flattened particles of tin it may contain, and the fine material carefully washed to recover the fine particles. After drying the tin is weighed. The produce is stated in parts of 20, or cwts. per ton. Thus, "produce 14" means 14 cwts. per ton, or 70 per cent. The residue obtained by washing may be fused into a prill in a clay crucible with sodium carbonate before weighing.

The quality of the metal is judged by remelting the tin, generally in an iron ladle, and pouring it at as low a temperature as possible into a marble mould. If pure, the surface remains unfrosted on solidifying. Impure tins crystallize, or become frosted "stain," on cooling.

If the metal is very impure, such as would be produced from ores containing much iron, copper, lead, zinc, antimony, etc., either as oxides, arsenides, or sulphides, it will melt only with difficulty in an iron ladle over an ordinary fire. In extreme cases it will not become more than pasty. No easy refining method being possible, it is necessary, in assaying ores, not only to state the amount of tin produced, but also its purity, as, by the reduction of foreign metals,

two samples may yield apparently equally good results, but vary greatly in value. An expert assayer can, by experience, judge of the nature of the impurity, and form a fair idea of the amount present.

This method answers well for comparatively pure tinstones only. With siliceous ores it yields low, and with ores containing foreign metals high results.

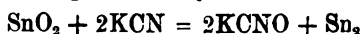
Assay of Tinstone with a little Siliceous Gangue.—With siliceous ores the charge consists of—

20	grms. tinstone
5	„ anthracite culm
15	„ carbonate of soda
3	„ lime or fluor spar

This method is useful for rich ores, without vanning, or for partially vanned samples, and yields good results. Another method is to run down the powdery residue obtained as in the Cornish method, with carbonate of soda, lime, and borax.

Ores containing mispickel and wolfram must first be digested with aqua regia to remove iron, copper, arsenic, etc., and to decompose the wolfram. After washing, the residue is treated with ammonia, to dissolve tungstic acid. The dried residue is then assayed as usual. Tin oxide is insoluble in the acid.

Assay by Fusion with Potassium Cyanide.*—Tin oxide is readily reduced by heating with potassium cyanide.



Weigh out 10 grms. of the finely powdered and dry sample and 40 grms. of powdered potassium cyanide. The ore must be vanned, if necessary, digested with hydrochloric and nitric acids, as above, washed, and dried. Stream tin and dressed ore do not require this treatment, unless associated with metallic compounds reducible by potassium cyanide. Put about 10 grms. of cyanide at the bottom of a crucible. Mix the ore with about 20 grms. of cyanide, and transfer the mixture to the crucible, and cover with the remainder of the cyanide. Place the crucible in a furnace at a *dull red heat*, and heat for about 25 minutes, taking care that the temperature does not get high enough to volatilize the cyanide, which will be shown by the assay giving off white fumes. Heat more strongly for a minute or two, and pour into a mould, or allow the crucible to cool and break it. Detach the button. Crush the slag and dissolve it in water. Collect any tin that is left and weigh.

This method is an excellent one. While heating, the pot must be

* This is by far the best method of assay.

covered and kept heated to the top, and care must be taken not to overheat.

Tin ore containing tungsten or wolfram may be assayed by this method.

Assay of Siliceous Tin Ores and Slags.—Owing to the great affinity of tin oxide for silica, it is extremely difficult to completely reduce it in the presence of that substance. Very prolonged exposure at the highest temperatures to reducing agents will effect the reduction. Black flux produces no separation of tin from tin slags, and even with un-siliceous materials, containing 80 per cent. of tin oxide, the loss of tin by that method of assay is often 20 per cent.

Method I.—25 to 125 grms. (according to richness) of the very finely pulverized material is vanned on a shovel, and the resulting heavy matters assayed as directed for ores free from or containing little silica.

Method II.—This method depends on the fact that tin is displaced from silicates by iron. The reduced tin will, at high temperatures, alloy with the excess of iron. The charge consists of—

- 25 grms. pulverized ore or slag.
- 12·5 ,, ferric oxide.
- 6 to 7 ,, fluor spar.
- 6·25 ,, finely powdered charcoal or anthracite.

The charge, after admixture, is transferred to a crucible, covered with a lid, and heated for 30 minutes at a dull red heat. Afterwards the temperature is raised nearly to whiteness, and the heat continued for another half-hour. The pot and its contents are removed from the fire, allowed to cool, and afterwards broken to obtain the button. This is treated by wet assay.

In dealing with Tin Slags, iron filings may be added direct, the charge being made up as follows :—

- 25 grms. slag.
- 5 ,, iron filings and a little fluor spar.

The fusion is conducted as before.

WET METHODS OF ASSAY.

Tin in Alloys.—In determining tin in alloys, advantage is taken of the formation of insoluble metastannic acid when the alloy is treated with strong nitric acid. No difficulty is experienced in thus separating it from other metals, except antimony. See Type-metal. Any phosphorus

present is, however, retained by the tin oxide. See Analysis of Phosphor Tin and Phosphor Bronze. In determining tin in bronzes, hard-head, and in alloys generally, take from 1 to 2 grms. of drillings or turnings in a No. 5 beaker, cover with 20 c.c. dilute nitric acid (sp. gr., 1.2), and heat till action ceases. Evaporate nearly to dryness. Dilute with about 50 c.c. water, and boil briskly for a few minutes. Let settle, decant through a filter; wash thoroughly, first with very dilute nitric, and afterwards with hot water. Dry the precipitate, detach as completely as possible from the filter paper, and put aside. Burn the paper in a weighed porcelain crucible, moisten the ash with nitric acid, and evaporate cautiously to dryness, to reconvert any reduced tin to stannic oxide. Add the main portion of the precipitate, ignite, and weigh as SnO_2 . Factor for tin = 0.7868.

Assay of Tin in an Ore.—The difficulty in estimating tin in ores by wet methods lies in the insolubility of the tin-oxide. It may be rendered soluble either by reduction to metallic tin, (1) by heating in a current of hydrogen, (2) by heating with carbon, or (3) by fusion with potassium cyanide.

Domeyko's Method modified.—Five grammes of the ore are calcined on a scorifier, and then digested with 25 c.c. hydrochloric acid in an evaporating dish. When the action has ceased, a few drops

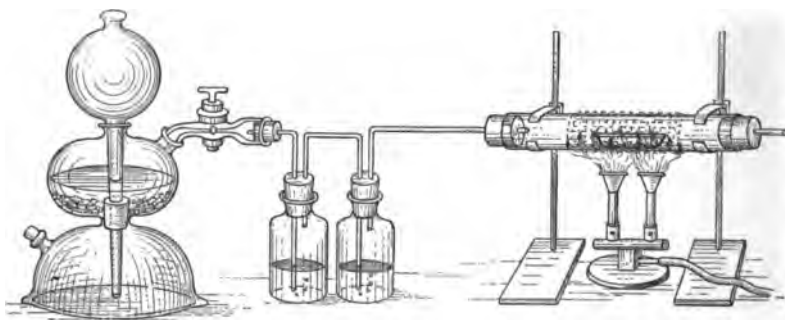


FIG. 80.

of nitric acid are added, and the solution boiled till red fumes are expelled. The residue is washed by decantation, and dried. It is transferred to a porcelain boat, and heated in a combustion tube about 1 ft. long, in a current of dry coal gas or hydrogen (freed from sulphur and arsenic by passing the gas through silver nitrate and caustic soda) for about 45 minutes, till completely reduced (Fig. 80). The tube is allowed to cool down while the gas is passing. The heating is best done in a combustion or tube furnace, but a couple of good

bunsens, with flat flames, answer well. The tube should be wrapped in wire gauze, and supported at the ends. If bunsens are used, a couple of bricks are placed one on each side, and the tube covered with a tile.

When cool, the boat and its contents are transferred to a beaker, and treated with hydrochloric acid till the tin is dissolved. A crystal of potassium chlorate, or a little potassium permanganate solution, aids the solution of the tin by forming stannic chloride. When solution is complete, the liquid is boiled, diluted to about 75 c.c., insoluble matters filtered off, a rod of zinc introduced, and allowed to stand till the tin is completely precipitated as metal. Decant through a filter, and wash well. Wash back any tin on the filter into the beaker, then detach the tin from the zinc, and remove the surplus of the latter metal. The tin may be weighed on a tared filter.

It is, however, better to convert the tin into stannic oxide by treating it with 20 c.c. dilute nitric acid, and proceeding as for alloys.

Instead of reducing in hydrogen, the ore, after purification, may be mixed with 2 grms. of finely powdered charcoal, and heated in a small clay crucible, lined with carbon, to effect the reduction (see p. 167), or by fusion with cyanide (Hart).

If antimony be present, it will, of course, be precipitated by the zinc. It may be separated by dissolving the precipitated metals in hydrochloric acid, with the addition of a few drops of nitric acid, boiling the solution and introducing a piece of clean iron, by which antimony is precipitated; whereas tin salts are only reduced to the stannous condition. The tin can then be precipitated by zinc as above.

VOLUMETRIC ESTIMATION.

Volumetric processes for the determination of tin depend on the conversion of the stannous into stannic salts by oxidizing agents. Potassium permanganate and bichromate are employed. It may also be estimated by potassium ferrocyanide.

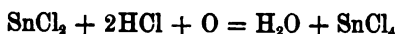
Estimation of Tin by Potassium Ferrocyanide.—The preparation of the solution and precipitation of the tin by zinc is proceeded with as above. The tin sponge is very carefully washed to completely remove zinc salts, finally, with weak ammonia; transferred to a flask fitted with a Bunsen valve (see p. 173), and dissolved in hydrochloric acid yielding stannous chloride. The solution is diluted to 150 c.c.

with freshly boiled water, and titrated with standard potassium ferrocyanide solution (p. 238), or with a solution containing 15.61 grms. of the salt per litre (1 c.c. = 0.01 gm. tin). The end of the reaction is determined on a spot plate, with ferric chloride as indicator.

Or an excess of the standard ferrocyanide may be added to the solution, and the excess estimated by potassium permanganate.

Copper, if present in the solution, is removed along with antimony and bismuth in the digestion of the solution with iron prior to precipitating the tin with zinc, while iron salts being in solution are removed by washing.

Estimation of Tin with Standard Bichromate of Potassium (Direct Process).—Stannous salts in presence of hydrochloric acid are converted by oxidizing agents into stannic compounds.



The standard solution of potassium bichromate employed in estimating iron may be used. Its tin equivalent will be found by multiplying the iron value by 1.0536.

The precipitated tin is dissolved, as before, in a flask fitted with a valve, the solution diluted to 150 c.c. with freshly boiled water, and titrated, using iodized starch as an indicator on a spot plate or paper till a blue colour appears.

Preparation of Iodized Starch.—Grind 0.5 gm. of starch with water in a mortar, and add the cream to 300 c.c. boiling water. To the solution add 5 grms. of potassium iodide and let cool. This solution may be used on the spot plate, or filter paper may be saturated with it and hung up to dry out of contact of chemical fumes. When dry, it is cut into suitable pieces and stored in a tightly-stopped bottle.

Indirect Method.—In this case the tin is made to act as a reducing agent on ferric chloride, and the ferrous chloride produced determined by titration with potassium bichromate, or the unreduced ferric chloride is estimated by stannous chloride. See Iron, p. 178.

The ferric chloride solution is made by dissolving 60 grms. of the salt in water, adding a few drops of hydrochloric acid, and diluting to a litre. The strength is determined by titration with potassium bichromate.

The tin is precipitated as before by zinc, well washed, transferred to a flask fitted with a valve, 100 c.c. of ferric chloride solution added, and warmed till dissolved. The solution is then titrated with the standard bichromate solution, using a potassium ferrieyanide indicator. See Iron, p. 177.

Correct results are not obtained by the indirect method unless the ferric chloride solution is dilute, in which case the action is slow.

Estimation of Tin in Bronze and Phosphor Bronze.—Take two grms. of the alloy, dissolve in 20 c.c. nitric acid, evaporate nearly to dryness, and dilute to 100 c.c. Boil up for a few minutes, let settle, decant through a filter, wash by decantation, and finally, on the filter. Dry the precipitate, and proceed as directed p. 226.

If the alloy contains phosphorus, the precipitate, after drying, must be mixed with about twice its weight of potassium cyanide and a little carbonate, and added in small quantities to a little cyanide fused in a *porcelain* crucible over a Bunsen burner and heated till reduction is complete. The mass, after cooling, is boiled with water, and the resulting tin dried and weighed.

Estimation of Tin in Phosphor Tin.—Take 1 grm. of the alloy, treat with 20 c.c. aqua regia, and evaporate till nitrous fumes are completely expelled, adding a little more hydrochloric acid if necessary. Dilute to 100 c.c., saturate with sulphuretted hydrogen while hot, filter, wash, and dry the precipitate, transfer it to a weighed crucible, and carefully ignite the tin sulphide over the bunsen, or in the muffle, to SnO_2 . Add a little ammonium carbonate or nitrate, and again ignite before weighing.

The filtrate from the sulphuretted hydrogen contains the phosphorus as phosphoric acid, which may be readily estimated by precipitation with magnesia mixture (see p. 358).

Estimation of Tin in Tinstone and Black Tin.—Very siliceous tinstone must be concentrated by vanning till the percentage of tinstone reaches 30 to 40 per cent. The residue must be dried, roasted in a muffle, and re-washed, taking care to lose no tinstone.

Two grms. of rich tinstone or of black tin may be taken and treated direct.

The residue or sample is washed into an evaporating basin and digested with 20 c.c. hydrochloric acid for 10 to 20 minutes, a few drops of nitric acid being added towards the end. The clear liquor is decanted through a filter, and the residue washed by decantation, first with dilute nitric acid, and finally with ammonia. Any particles on the filter are washed back into the basin, and the residue dried, ignited, and weighed.

It is powdered in an agate mortar, and the whole, or a weighed portion, reduced by heating in a current of hydrogen (p. 226), and the tin obtained dissolved in 10 c.c. strong hydrochloric acid. A piece of bright iron wire is introduced for a few minutes, and on removal, washed. A rod of zinc is then added, and after standing the precipi-

tated tin collected, dissolved and estimated by one of the methods given above.

Estimation of Tin in Hardhead.—This determination is complicated by the presence of large quantities of arsenic, and shots of metallic tin, etc. The method of procedure is as follows:—Take a large sample, say, 100 grms., of the roughly powdered hardhead. Powder the sample as completely as possible, and sift through an 80 sieve, reserving the coarse particles, which contain the metallic tin. Weigh each portion. The tin must be separately determined in both the fine powder and coarse grains.

Examination of Metallic Portion.—Take 1 grm. of the metallic residue, dissolve in 15 c.c. aqua regia, and evaporate nearly to dryness. Add a little HCl, and a clean strip of iron, to remove arsenic, copper, and antimony. Remove and wash the iron. If necessary, filter through glass wool, and wash. Add a rod of pure zinc to the solution, and let stand; collect the precipitated tin, and determine as before.

Examination of Powder.—Weigh out 5 grms. of the powder, roast in a muffle till as free from arsenic as possible, and re-weigh. Take one-fifth of the residue equivalent to 1 grm. of the powder (a grm. of the substance may be taken without roasting, but it is more difficult to treat). Dissolve it in 10 c.c. aqua regia, and evaporate to pastiness. Take up with 5 c.c. dilute hydrochloric acid, add 100 c.c. water, and saturate while hot with sulphuretted hydrogen. Filter and wash rapidly with hot water. Wash the precipitate into a beaker, and warm with potassium sulphide and a little sulphur and caustic potash, to dissolve the arsenic and tin sulphides. Filter off any insoluble lead, copper, and bismuth sulphides. Dilute to 150 c.c., and saturate the liquid with sulphurous acid gas. Evaporate to one-third its bulk, till SO_2 is completely expelled.* The tin sulphide is precipitated; arsenic sulphide remains in solution. Filter thoroughly, wash with a saturated solution of common salt, and afterwards with weak ammonium acetate, slightly acidified with acetic acid. Dry, ignite to oxide, and weigh. Factor for tin = 0.7868.

Any antimony present is precipitated with the tin. Its presence may generally be observed in the original precipitate by sulphuretted hydrogen, to which it imparts a red colour. It may be separated by dissolving the precipitate in hot strong hydrochloric acid and precipitating by iron as previously described.

Calculation of Results.—Suppose a sample on crushing gave 14.5 grms. metallic particles, and 85.5 grms. of fine powder.

* Tin and antimony sulphides are insoluble in potassium bisulphite.

The metallic particles are found to contain 95·6 per cent. of tin

The powdered portions are found to „ 20·3 „ „

$$14·5 \times 95·6 = 1386·20$$

$$85·5 \times 20·3 = 1735·65$$

$$3121·85$$

$$\frac{3121·85}{100} = 31·218 \text{ per cent. of tin}$$

Estimation of Tin in Slags.—Treat 2 grms. of the very finely powdered tin slag (ground in an agate mortar, and sifted) with 20 c.c. hydrochloric acid in an evaporating basin, and heat to boiling till decomposition is complete, then add to the boiling solution a few drops of nitric acid, and boil. Dilute to 50 c.c., filter off insoluble matter, and wash thoroughly with hot water. Saturate the solution with sulphuretted hydrogen, let settle and filter. Wash and dry the precipitate. Transfer to a weighed wide porcelain crucible, and roast to oxide in muffle, or first over bunsen, and then over the foot blowpipe, adding a little carbonate of ammonia at the end. The amount of tin is generally about 7 per cent.

If the slag contains shots of tin, they must be separated by sifting, weighed, and the proper proportion allowed to the assay. If necessary, they must be assayed, and the calculation made as in hardhead.

The above remarks apply to “glass,” or run slags. The unfused residue, commonly called slag in the works, consists of unburnt anthracite, pellets of slag, and shots of tin. To assay this, it is necessary to first burn off the anthracite from a weighed portion, and treat the residue as for slag, first separating the shots of tin, and then assaying the slag.

For complete analysis of slags, see Part III.

ZINC.

THE substances in which the estimation of this metal is usually required are—

Ores { Oxidized—Zincite, calamine (smithsonite), franklinite, hemimorphite (electric calamine), willemite, and other silicates.
Sulphurized—Blende, zinciferous galenas, zinciferous silver and gold ores.

Mattes.

Slags.

Fume.

Alloys.

Galvanizer's waste.

Zinc Ores—Red Zinc Ore, Zincite, Spartalite.— $\text{Zn}(\text{MnFe})\text{O}$ has an almost ruby red colour, is transparent to translucent, and is generally closely associated with franklinite. See Iron. The crystals are rhombic, fairly hard, heavy (sp. gr., 5.4). It gives a white streak, and is brittle; is infusible, but gives zinc and manganese reactions before the blow-pipe, and dissolves in nitric acid.

Calamine (Smithsonite).—Zinc carbonate, ZnCO_3 , occurs crystallized in rhombohedra, but more often in massive, stalactitic, reniform, or encrusting forms. The colour varies from white to brown. The streak is white. It is brittle, and has a sp. gr. about 4.4. Soluble in hot acid, with effervescence. Gives zinc reaction on charcoal. See below. Infusible before the blow-pipe.

Hemimorphite (Electric Calamine).—Hydrated silicate of zinc somewhat resembles the above, and is often associated with it. It is, however, somewhat softer and less heavy. It dissolves in sulphuric acid without effervescence, and leaves gelatinous silica; it is infusible before the blow-pipe, though it often intumescs and glows; becomes electrified when heated.

Willemite is another silicate crystallizing in the rhombohedra system, which behaves similarly.

Zinc Blende.—**Black jack**, sulphide of zinc, often occurs crystalline in forms belonging to the cubic system, with a perfect dodecahedral cleavage, also in brittle cleavable masses. Lustre, resinous, to sub-metallic in black varieties. Colour, varies from yellowish to black. Streak, white. It is translucent to opaque. Hardness, 3·5–4. Sp. gr., 4–4·1. Distinguished by its brittleness, infusibility, perfect cleavage, waxy lustre, hardness, and sp. gr., from hornblende, tinstone, garnet, etc. After calcination it gives zinc reactions before blow-pipe.

Double sulphides of lead and zinc (impure galenas) occur, containing varying percentages of zinc. They may generally be distinguished from pure galena by their darker colour and lower sp. gr. Also by the white fumes and incrustation which they yield when heated on charcoal before blow-pipe. The estimation of zinc in these ores is important, owing to the difficulty of removing the zinc in smelting such of them as are argentiferous.

Slags.—In these the zinc exists as silicate. Owing to the difficult fusibility of zinc silicate, it is generally fluxed by slags, rich in iron. Such slags contain silicate of iron, and are consequently black. They seldom contain more than 15 per cent. of zinc.

Fume and flue dust contain zinc, as metal, sulphide, and oxide. Considerable quantities of zinc oxide are deposited in the dust chambers of iron and other blast furnaces engaged in smelting zinciferous ores, in the form of a whitish grey powder.

Zinc dust (fume) from the fume condensers contains zinc as metal and oxide. It is generally a grey pulverulent mass.

Alloys.—Brass, German silver, some bronzes, and pattern alloys.

Galvanizer's Waste.—Various products consisting of (1) zinc chloride and ammonium chloride, (2) a hard alloy with iron.

Spelter.—This is the commercial name of zinc in cakes. It usually contains tin, lead, arsenic, antimony, and iron, and sometimes other impurities.

REACTIONS FOR ZINC.

Dry Reactions.—Zinc oxide heated in a closed tube turns yellow, but becomes white again on cooling. Zinc carbonate gives off CO_2 , leaving zinc oxide, which behaves as above.

Mixed with fusion mixture, and heated on charcoal in the reducing flame, a white film deposits on the charcoal beyond the assay. This

is non-volatile in the oxidizing flame, and is tinged green if moistened with cobalt nitrate, and reheated in the oxidizing flame.

Wet Reactions.—Pure zinc is completely soluble in dilute hydrochloric acid. Impure zinc leaves a residue consisting principally of lead.

1. Solutions containing zinc give no precipitate with sulphuretted hydrogen in hydrochloric acid solution.

2. Sulphuric acid gives no precipitate.

3. Ammonia gives a white precipitate of zinc hydrate, which dissolves in excess, or in acids.

4. Sodium hydrate (caustic soda) behaves similarly.

5. Ammonium carbonate gives a white precipitate of zinc carbonate, soluble in excess and in ammonia.

6. Sodium carbonate gives a white precipitate of zinc carbonate, insoluble in excess.

7. Ammonium sulphide and sulphuretted hydrogen in alkaline solution give a white precipitate of zinc sulphide, readily soluble in hydrochloric acid, but *insoluble* in acetic acid.

8. Potassium ferrocyanide precipitates white zinc ferrocyanide, insoluble in dilute hydrochloric acid, even on warming.

Most of the salts of zinc are soluble compounds.

METHODS OF ESTIMATING ZINC.

Dry Methods.—Various methods of estimating zinc by dry methods have been proposed, none of which are reliable.

Twenty grms. of the finely powdered ore is roasted to remove sulphur, and heated to very bright redness in a muffle to decompose, and expel carbonic acid from any carbonates, and re-weighed. 10 grms. of the residue is intimately mixed with one quarter of its weight of powdered charcoal, or, better, anthracite (previously strongly ignited), and placed in a carbon crucible, covered with a carbon plug, and intensely heated for an hour or so, till all zinc vapour is expelled. The closely covered crucible is allowed to cool down, and the residue carefully removed and weighed. The residue is then placed on a scorifier and carefully calcined to completely remove the excess of carbon, and re-oxidize iron and other non-volatile metals that may have been reduced. The calcined residue is weighed. The difference in weight before and after experiment = ZnO.

Original weight of sample = 20 grms.

Weight of sample after roasting = 15·84 „

Weight of roasted sample taken = 10 „

Weight of calcined residue = 1·35 „

Hence

$$10 - 1.35 = 8.65 \text{ grms. ZnO in roasted sample}$$

Then

$$8.65 \times \frac{15.84}{10} = 13.701 \text{ grms. ZnO in 20-grm. original sample}$$

Percentage of zinc oxide—

$$20 : 100 :: 13.701 = 68.505$$

Percentage of zinc—

$$\text{Factor} = 0.8026$$

$$68.505 \times 0.8026 = 54.982$$

If blendes are being treated, care must be taken to finish the roasting at a high temperature, so as to decompose the sulphate formed during the earlier stage.

WET METHODS.

Zinc and almost all its compounds are readily soluble in acids.

Alloys are best dissolved in nitric acid, as the tin and antimony are then left as insoluble oxides (see p. 215). After filtering, the nitric acid is removed from the solution by evaporation with hydrochloric acid.

In dissolving blendes, proceed as directed p. 79. Zinciferous galenas are best treated as for galena (p. 63, Method II.). After filtering off insoluble residue and lead sulphate the zinc remains in the filtrate.

Preparation of Solution.—The most usual methods for determining zinc are only applicable to solutions from which the other heavy metals are absent. Hence, at the commencement, foreign metals must be removed.

For ores which do not contain copper, the simplest procedure is to add to the solution in acid a large excess of ammonia, and then ammonium carbonate. The zinc remains in solution while the foreign metals, except copper, are precipitated. There is a great tendency for the precipitate to carry down notable amounts of zinc, which would cause low results to be obtained; but by dissolving the precipitate and precipitating a second or even a third time, this may be, to a large extent, overcome.

For general purposes the best plan is to saturate the hydrochloric acid solution with sulphuretted hydrogen. Filter and wash the precipitate with water containing sulphuretted hydrogen. If much

copper be present, this precipitate must be dissolved and again precipitated, as it has a tendency to carry down zinc. Mix the filtrates, boil off sulphuretted hydrogen, and peroxidize the iron with nitric acid. Add excess of ammonia and a little ammonium carbonate; boil, and filter. If a large precipitate is produced, it must be dissolved, and re-precipitated. The filtrate contains the zinc.

This method is applicable in all cases, save in the presence of much iron (as in galvanizer's waste), phosphates, or much lime. In such cases phosphates and iron must be removed by neutralizing the solution, from which sulphuretted hydrogen has been expelled, with ammonia, and precipitating as basic acetate by sodium or ammonium acetate (see p. 353). If much lime is present, the zinc must first be precipitated as sulphide by adding ammonium sulphide to or by passing sulphuretted hydrogen through the alkaline solution. The precipitate is dissolved in hydrochloric acid, the solution boiled to expel sulphuretted hydrogen, and carefully neutralized with caustic soda.

Estimation of Zinc by precipitation as Carbonate.—From 1 to 2 grms. of the substance is dissolved in nitric or hydrochloric acids, evaporated to dryness, taken up with a little hydrochloric acid diluted to 100 c.c. (or more if much lead and copper and little zinc be present), and saturated with sulphuretted hydrogen. The precipitate is filtered and washed. The filtrate is boiled until sulphuretted hydrogen is expelled, a little nitric acid added to peroxidize any iron present, and the iron, etc., removed as basic acetate by neutralizing the solution, adding excess of sodium acetate, and heating to boiling. The precipitated basic acetates are filtered and washed. The filtrate is then made alkaline and saturated with sulphuretted hydrogen. The precipitate of zinc sulphide, etc., is allowed to settle, filtered, and washed. It is then dissolved in dilute hydrochloric acid, and sodium carbonate solution added in *slight* excess. The solution is then boiled, filtered, the precipitate thoroughly washed, dried, strongly ignited, and weighed as ZnO. It should be again ignited and re-weighed till the weight is constant. The final ignition must be at a high temperature. The precipitate must be removed as completely as possible before burning the filter paper, or it may be partly reduced and loss occur by volatilization. Thorough washing of the precipitate is important, as zinc carbonate is liable to carry down with it sodium salts from the solution. The zinc precipitate contains after ignition 80.26 per cent. of zinc.

By this method any manganese present is precipitated with the zinc by sulphuretted hydrogen, the manganese sulphide being dissolved when the precipitate is treated with hydrochloric acid, and precipitated

with the zinc on addition of sodium carbonate. The zinc oxide is discoloured if much manganese be present. The manganese is estimated by dissolving the precipitate in a little concentrated hydrochloric acid, adding caustic soda in excess, boiling, diluting largely, and filtering. The precipitate is washed, dried, ignited, and weighed as Mn_2O_3 .

Estimation of Zinc in Brass.—Weigh out 1 grm. of the brass. Dissolve in 10 c.c. nitric acid in an evaporating basin covered with a funnel. Evaporate to dryness. Take up with a little dilute hydrochloric acid, and wash into a beaker. Dilute to 100 c.c., warm, and saturate with sulphuretted hydrogen. Let settle, filter, and wash the precipitate with water containing sulphuretted hydrogen; boil off sulphuretted hydrogen, add a few drops of nitric acid, and boil. To the solution add sodium carbonate till alkaline, boil, and treat precipitate as above.

NOTE.—Any iron will be precipitated with the zinc. If necessary, the precipitate may be dissolved in HCl, and the iron precipitated with ammonia, weighed, and the weight of the oxide deducted. It is unsatisfactory to remove iron by ammonia before precipitating zinc with sodium carbonate, unless the zinc be separated as sulphide.

Estimation of Zinc in Smithsonite or Calamine.—Dissolve 1 grm. of the ore in 15 c.c. strong HCl and evaporate to dryness (most calamines contain some silicate, and evaporation is necessary to render the silica insoluble). Take up with water, acidify slightly, warm and saturate with sulphuretted hydrogen. Filter and wash the precipitate. Boil off sulphuretted hydrogen and peroxidize iron by boiling with a little nitric acid. Neutralize carefully with ammonia (see p. 353, Estimation of Manganese in Iron and Steel), add (2 to 3 grms.) ammonium or sodium acetate, and boil. Let settle, filter, and wash the precipitated basic iron acetate. Make slightly alkaline with ammonia, heat to boiling, and saturate with sulphuretted hydrogen. Boil for ten minutes or until the precipitate settles readily, and test whether precipitation is complete by adding 1 drop of ammonium sulphide to the clear liquor. Let settle, decant through a filter, wash by decantation and then on the filter. Wash the precipitate back into the beaker with dilute hydrochloric acid, and warm till dissolved. Boil off sulphuretted hydrogen and add slight excess of sodium carbonate, and proceed as before.

NOTE.—This is a general method serving under almost all conditions. The only interfering metal is manganese, which must be dealt with (see p. 193.)

Determination of Zinc as Phosphate (Tamm's Method).—Di-sodium phosphate (ordinary sodium phosphate), if added to the hot solution and allowed to stand on the hot plate for a few minutes in presence of ammonia and ammonium chloride or acetate, precipitates zinc as the zinc-ammonium phosphate, $ZnNH_4PO_4$. This precipitate settles, filters,

and washes well. It is not absolutely insoluble, but on standing for some hours, or by vigorously shaking the assay, all but a trace is thrown down. The precipitate should be collected on a tared filter, dried at 100° C., and weighed, as some loss of zinc occurs on ignition to pyrophosphate.

The precipitate has a great tendency to adhere to the sides of the beaker as a thin film. If this is difficult to remove with the policeman, dissolve it in a few drops of dilute HCl, reprecipitate and filter. This adhesive tendency is diminished by adding a large excess of sodium phosphate. The solution should have a faintly alkaline reaction. The washing should be continued till the washings give no precipitate with silver nitrate. The filtrate should be tested with ammonium sulphide to ensure complete precipitation of the zinc.

VOLUMETRIC METHODS.

Oxalate Method (Leison's Method modified).—Zinc is completely precipitated in alkaline or neutral solution by ammonium oxalate in presence of alcohol.

The precipitate is difficult to filter in the ordinary manner, but may be collected on a specially prepared sand filter. The funnel is plugged lightly with glass wool, and a layer of fine sand, half an inch deep, is put above it. If the filter pump is to be used, a little asbestos (p. 46) should be added.

After preparing the zinc solution and separating foreign metals, add a slight excess of ammonia, and a large excess of ammonium oxalate. Then add alcohol at least equal in volume to the solution. Shake well, and let stand. Filter, wash with alcohol and water till free from oxalate, and dry in a water oven.

Determination of the Zinc.—Place the funnel over a conical flask, raise the glass wool plug, and wash down the precipitate, sand, etc., with hot dilute sulphuric acid. A little strong acid is added and the flask warmed. This liberates the oxalic acid, which is estimated by titration with standard permanganate of potash (p. 203). The iron equivalent of the permanganate solution multiplied by 1.723 gives the zinc equivalent.

Estimation by Potassium Ferrocyanide.—This is the most simple method of determining zinc for assay purposes, and is at the same time accurate, providing it is carried out under uniform conditions of temperature, and amount of free acid.

Zinc ferrocyanide is insoluble in dilute acetic or hydrochloric acids,

and the presence of excess of the reagent is readily indicated by means of uranium salts.

This method may be used as a direct process, the zinc solution being titrated with a standard solution of potassium ferrocyanide, or an excess of a standard solution of potassium ferrocyanide may be added to the zinc solution, and the excess determined by titration with standard potassium dichromate, using ferric chloride as an indicator. The direct method is most commonly employed.

Standard Solution of Potassium Ferrocyanide.—Dissolve 43·2 grms. of the pure salt in water, and dilute to one litre. Each c.c. of the solution = 0·01 gm. Zn.

Standard Zinc Solution.—Dissolve 10 grms. of pure zinc in 100 c.c. dilute hydrochloric acid (1 : 1), and dilute to a litre. 1 c.c. of this solution = 0·01 gm. Zn.

Uranium Acetate Solution.—Dissolve 0·5 gm. in 100 c.c. of water. This may be either added to the assay solution or used on a spot plate. The latter is the better method. Test the reaction between the ferrocyanide and uranium solutions before proceeding with the estimation.

Standardizing the Solution.—Measure out 50 c.c. of the standard zinc solution into a flask by means of a pipette, neutralize with ammonia, then add 5 c.c. strong hydrochloric acid, dilute to about 100 c.c., and heat nearly to boiling. Add a few drops of the uranium acetate solution. Titrate while hot with the ferrocyanide solution till the brown colour which first forms disappears only sluggishly on stirring. Then continue the titration, testing with uranium on spot plate until brown colour appears. Repeat and calculate standard (see p. 51). The ferrocyanide solution does not keep very well, and must be standardized for each batch of determinations.

Determination of Zinc in Blende by above Method.—Weigh out 0·5 gm. of the finely powdered and sifted ore, and transfer to a conical beaker. Cover with dilute nitric acid (1 : 1), and warm (not boil) for some time till the ore is decomposed. Then add dilute hydrochloric acid, and evaporate till nitric acid is completely expelled. Add more hydrochloric acid, and again evaporate if necessary. If copper be present, it must be precipitated by saturating the solution with sulphuretted hydrogen, and filtering and washing the precipitate. Boil off sulphuretted hydrogen, add ammonia to excess, and a little solid ammonium carbonate. Filter and wash the precipitate. If it is bulky, dissolve in hydrochloric acid, reprecipitate, and mix the filtrates. Neutralize with hydrochloric acid, add 5 c.c. in excess, and dilute to 100 c.c. Heat nearly to boiling, and titrate as in standardizing.

Lead does not interfere if sufficient hydrochloric acid be present.

Estimation of Zinc in Calamine.—Weigh out 1 grm. of the calamine and dissolve in 20 c.c. HCl. Add a few drops of strong nitric acid and boil to peroxide the iron, and evaporate to dryness. Dissolve in dilute HCl (1 : 4) and remove other metals from the solution as directed above. Neutralize, dilute to 100 c.c., and make acid with hydrochloric acid. Heat nearly to boiling, add a few drops of the uranium acetate solution, and run in ferrocyanide solution from burette slowly, and with continuous stirring. White zinc ferrocyanide is precipitated. When precipitation is nearly complete, the brown colour produced by the presence of the uranium acetate only disappears slowly on stirring. At this stage, the assay should be tested by bringing a drop in contact with a drop of the uranium solution on a spot plate, as the indication is more delicate and definite. The colour seldom appears instantly.

Notes.—The process is not affected by ammonium salts. The final reaction is more decided in hydrochloric than in acetic solution, but takes a little longer to act. Within reasonable limits excess of hydrochloric acid does not affect the result. The reaction takes place more readily in a hot solution. In determining zinc in brass and other cupreous substances, the copper is best precipitated electrolytically.

A method for the removal of copper from the solution after treatment with ammonia—indicated by the blue colour—is to acidify with sulphuric acid and add aluminium foil, and leave till the colour is destroyed.

Cadmium and bismuth, if present, interfere, and must be removed by sulphuretted hydrogen in acid solution. Nickel and cobalt must be removed by precipitation of the zinc as sulphide in acetic acid solution (see p. 192). The amount of hydrochloric acid in excess, and the temperature of titration, about 80° C., are the most important considerations in the success of the assay.

A variation of this method is conducted as follows:—Besides the standard solution of potassium ferrocyanide and the uranium indicator, a saturated solution of potassium chlorate in nitric acid, and a 10 per cent. solution of ammonium chloride, are employed.

Blendes, calamines, and electric calamine are dissolved in the chlorate solution, 1 grm. of the ore in 25 c.c. of the solution.

This is warmed till the chlorous fumes disappear, and evaporated to a paste. This precipitates the manganese as MnO_2 . The liquid is diluted to 25 c.c. with water, 7 grms. of ammonium chloride (70 c.c.) added, and then 15 c.c. strong ammonia. It is well stirred and boiled for a few minutes. The precipitated ferric hydrate, etc., is filtered off. If in large quantity, it must be retreated from the beginning, as it will contain zinc.

The filtrate (or mixed filtrates if twice treated) is diluted to 200 c.c., and after neutralization with hydrochloric acid, the necessary excess of acid added, heated to 80° C., and titrated as before. Some workers use a less excess of hydrochloric acid, only 2 c.c.; but in presence of lead this is not sufficient, as ferrocyanide of lead may be precipitated.

Willemite and other refractory ores give low results by this method. If it be used, it must be preceded by a preliminary evaporation of the ore to dryness with aqua regia or hydrochloric acid. All the hydrochloric acid must be removed before treating with the chlorate solution, or manganese will not be completely precipitated.

Franklinites and other manganiferous ores are best treated by fusing 1 grm. with 10 grms. sodium and potassium carbonates and $\frac{1}{2}$ grm. of KNO_3 for an hour, or with potassium bisulphate. The mass is dissolved in HCl, with the aid of heat, if

necessary, evaporated to small bulk, a very little KClO_3 added, and chlorous fumes boiled off. The solution is diluted to 100 c.c. nearly neutralized, and the iron, etc., precipitated with barium carbonate free from alkaline carbonates.*

The BaCO_3 is added to the solution in a flask, with repeated shaking. The precipitate is filtered off and washed with cold water. The manganese is then precipitated as MnO_2 by bromine, thus:—The filtrate is acidified with 5 c.c. acetic acid, some sodium acetate added, and 5 c.c. bromine. After solution of the bromine, the liquid is heated nearly to boiling, and allowed to stand. The precipitated MnO_2 is filtered off and washed, the filtrate containing the zinc is neutralized with sodium carbonate, the necessary excess of hydrochloric acid added, heated to 80°C ., and titrated as before.

The sensitiveness of the uranium indicator may be determined thus:—200 c.c. of water, and 25 c.c. of the ammonium chloride solution, with the same excess of HCl , as is to be employed, are heated to 80°C ., and potassium ferrocyanide added till the colour that it is to be worked to is obtained on the spot plate. The amount of ferrocyanide solution thus used should be deducted from that used in every assay made with it.

Estimation of Zinc as Sulphide.—Zinc is completely precipitated from alkaline solution by sulphuretted hydrogen or sodium sulphide.

Standard Sodium Sulphide Solution.—Dissolve 17.3 grms. of caustic soda in water. Divide into two equal parts, and saturate one portion with sulphuretted hydrogen. Add the other half, and dilute to a litre, or dissolve 12 grms. of sodium sulphide in water, and make up to a litre.

Standard Zinc Solution.—See p. 238, or dissolve 44.15 grms. of pure zinc sulphate, and make up to a litre.

Nickel Indicator.—Make a dilute solution of nickel sulphate, add ammonia till strongly alkaline, and use on a spot plate.

Sodium Nitroprusside may also be used as the indicator. With alkaline sulphides it gives a fine purple coloration. It must be used on a spot plate.

Standardizing.—Take 25 c.c. of the zinc solution in a beaker and add ammonia till the precipitate redissolves. Then run in the sodium sulphide from a burette, with constant skaking, and test drops on spot plate. The titration is complete when the drop is just discoloured. Calculate the zinc value of the standard solution.

As in all other methods of determining zinc, it is necessary to remove foreign metals from the solution.

The solution of the material is prepared as before, but with even greater care, in order to eliminate other metals.

Assay of Zinc Dust.—Zinc dust or fume is the fine powder removed from the fume condensers, and consists of a mixture of finely divided zinc and zinc oxide. It is used as a reducing agent for manufacturing purposes in acid solutions, and is also resmelted.

The total zinc may be estimated by any of the ordinary methods, but for reduction purposes only the metallic zinc is of value. This

* This may be ensured by previously digesting the barium carbonate with barium chloride, and thoroughly washing.

may be determined by collecting and measuring the hydrogen evolved from a weighed quantity.

Estimation of Metallic Zinc by Reduction of Chromic Acid (Drewsen's Method).—Chromic Acid Solution.—Dissolve 40 grms. of pure potassium bichromate, or 27 grms. of chromic acid, and make up to 1 litre.

Standard Iron Solution.—Dissolve 200 grms. of ferrous ammonium sulphate in water, add 100 c.c. of sulphuric acid, and make up to a litre with boiled water.

Determine the iron value of the bichromate solution by titration (as described on p. 177) with ferricyanide indicator.

$$\text{Iron equivalent} \times \frac{64.9}{111.8} = \text{zinc equivalent}$$

Estimation.—Weigh out 0.5 gm. of the well-mixed sample, and place in a 300 c.c. flask. Add 100 c.c. of the chromic acid solution, then 10 c.c. dilute sulphuric acid (1 : 1). Shake well, and let stand a few minutes. Add 10 c.c. more sulphuric acid, and again let stand in a warm place till solution is complete. Titrate the excess of bichromate solution with the standard iron solution. This is the reverse of the estimation of iron, and the addition of the ferrous salt is continued till a blue colour appears.

$$100 \text{ c.c.} - \text{excess} = \text{quantity reduced by zinc}$$

$$\text{Iron equivalent of quantity} \times \text{by } \frac{64.9}{111.8} \times \frac{100}{0.5} = \text{percentage of zinc.}$$

Fresenius recommends the solution of the zinc powder in sulphuric acid, passing the hydrogen evolved, after thorough drying, over red-hot cupric oxide, and collecting the water formed in weighed calcium chloride tubes.

CADMIUM.

THIS metal closely resembles zinc in its physical and chemical properties, but differs from it in being precipitated by sulphuretted hydrogen from dilute hydrochloric acid solution, and is thus thrown down with the copper group.

It occurs only, to a very limited extent, generally associated with zinc. Most blendes and many calamines contain small quantities, sometimes up to 3 per cent. of cadmium.

The rare yellow mineral Greenockite is sulphide of cadmium, CdS . Cadmium being more volatile than zinc, comes over first in the reduction of cadmium-zinc ores. On coming into the air the vapour burns, forming brown fumes of CdO —the “brown blaze” of the zinc smelter.

Cadmium yellow is cadmium sulphide.

Some dental amalgams contain cadmium, and, electro deposited, it has been used as a preservative for iron in place of zinc. Its resistance to atmospheric action is high.

REACTIONS OF CADMIUM.

Wet Reactions.—In these cadmium resembles zinc, with the exception mentioned above, and that the hydrate is insoluble in caustic soda.

Hydrochloric acid produces no precipitate.

Sulphuretted hydrogen in hydrochloric acid solution produces a yellow precipitate of cadmium sulphide, CdS , insoluble in caustic soda or ammonium sulphide, but soluble in nitric or sulphuric acid. This precipitate is thrown down, even in the presence of potassium cyanide. See Copper.

Caustic soda produces a white precipitate insoluble in excess. When dried and heated it turns brown. Ammonia produces the same precipitate soluble in excess.

Ammonium sulphide precipitates the sulphide.

Dry Reactions.—Before the blow-pipe cadmium compounds give a brown incrustation on charcoal, which is volatile in the reducing flame.

Estimation of Cadmium as Sulphide.—**Preparation.**—The finely powdered sample, if a mineral sulphide, is treated with nitric and hydrochloric acid, as described for zinc (p. 235). Or if a carbonate,

or silicate, it is dissolved in hydrochloric acid, the solution evaporated to dryness, taken up with a little dilute hydrochloric acid, and the insoluble silica filtered off and washed. The solution, while warm, is saturated with sulphuretted hydrogen (if arsenic be present, a little sulphurous acid should be added and boiled off before passing sulphuretted hydrogen), allowed to stand in a warm place for some time, and the precipitate filtered and washed. Great care must be taken that the solution is not too strongly acid, or the cadmium will not be precipitated. This is a common source of error in cadmium determination. Sulphuretted hydrogen must be passed to complete saturation.

The precipitate is then washed down into a beaker and digested with sodium sulphide, for at least an hour. The solution is diluted, filtered, the residue washed, dissolved in dilute nitric acid, and ammonia added in excess. Any precipitate thrown down (Pb and Bi) is filtered off. If copper be present the solution will be blue. In that case, add potassium cyanide solution till it becomes colourless. It is then saturated with sulphuretted hydrogen, the precipitate collected on a tared filter, washed with water containing sulphuretted hydrogen, and finally with water, dried at 100° , and weighed as cadmium sulphide. The dry precipitate, after weighing, is treated with carbon disulphide to remove sulphur, and reweighed. For this purpose the paper must be wet with CS_2 , in which case it will filter. Factor for Cd = 0.7773.

In the absence of bismuth, the precipitate, after treatment with sodium sulphide, may be warmed with dilute sulphuric acid (1 : 5), the solution filtered off, and the residue washed. The filtrate contains the cadmium, and may be immediately precipitated as sulphide.

Estimation by Precipitation as Carbonate and Weighing as Oxide.—The sulphide, separated as above, is dissolved in nitric acid, and precipitated by sodium carbonate. The precipitate is then dealt with in the same way as zinc carbonate.

Volumetric Estimation.—Cadmium is estimated volumetrically by precipitating the metal as oxalate with oxalic acid and strong alcohol in an aqueous solution of a neutral salt. The solution may be prepared by solution of the sulphide in sulphuric acid as before and neutralizing with sodium carbonate. Ammonium oxalate is then added in large excess, and a volume of alcohol equal to that of the solution. The solution is shaken, allowed to stand for some time, and the precipitate filtered and washed with alcohol and water till free from oxalate. It is afterwards dried, dissolved in warm dilute sulphuric acid, and the oxalic acid estimated by titration with potassium permanganate. See Zinc.

ARSENIC.

ARSENIC may have to be estimated in the following bodies :—

Native arsenic.

White arsenic, As_2O_3 .

Orpiment, As_2S_3 .

Realgar, As_2S_2 .

Arsenical iron pyrites, mispickel, FeAsS , separately and in admixture with other ores.

Leucopyrite, Fe_2As_3 .

Smaltine, kupfernickel, chloanthite, cobaltite, and other cobalt and nickel ores.

Copper ores.

Speiss, regulus.

Iron precipitates (basic arsenate).

Green pigments (Scheele's and Schwemfurth's).

Shot alloy, and many metals.

Arsenites and arsenates.

Native Arsenic occurs to some considerable extent with a reniform, massive, or granular structure. The fresh fracture is almost tin-white, but tarnishes rapidly, becoming nearly black. The lustre is metallic. Hardness, 3·5. Brittle, fracture uneven to granular. Before blow-pipe, volatilizes without fusion, generally giving white fumes and garlic odour ; usually gives a white deposit on charcoal, which is very volatile in oxidizing flame. Some varieties contain antimony.

White Arsenic occasionally occurs native, as an incrustation, or in fine hair-like crystals associated with other arsenical ores. Artificial white arsenic is met with in two forms, as "glass" and "powder."

Orpiment.—Generally foliated. Crystals, rhombic. Cleavage, highly perfect. Sectile. Colour, fine yellow (King's yellow). Translucent. Lustre, pearly ; splendid on cleavages. Elsewhere resinous to dull. Hardness, 1·5–2. Sp. gr., 3·4.

Distinguished from yellow mica by the inelasticity of its plates and lower hardness. Gives garlic odour and white fumes when heated on charcoal.

Realgar.—Often crystalline, also massive. Crystals, monoclinic. Colour and streak, deep orange to red. Lustre, resinous. Transparent to subtranslucent. Hardness, 2.

Distinguished from crocoisite, wulfenite, etc., by the characteristic reactions for sulphur and arsenic.

Mispickel.—Crystals, generally in rhombic prisms, with modified ends. Also massive. Colour, almost silver-white, with slightly grey tendency. Tarnishes yellowish or light copper-colour. Streak, nearly black. Lustre, metallic. Fracture, uneven. Brittle. Hardness, 5.5–6. Sp. gr., 6.3. Gives arsenical fumes, and yields a globule of iron sulphide when heated on charcoal. Strongly heated in closed tube gives a sublimate of arsenic. Often contains cobalt. Is associated with silver, copper, lead, zinc, cobalt, and tin ores.

Other Arsenical Ores.—See Cobalt, Nickel, Silver, and Copper.

Speiss.—The arsenides of nickel and cobalt produced in the concentration of those metals. A heavy, crystalline or granular brittle body, with a submetallic uneven fracture of a white colour, inclining to pink. Gives arsenic reactions before blowpipe, and the residue gives reactions for nickel and cobalt, with borax. See Nickel.

Iron Precipitates.—These are obtained in the manufacture of nickel, and consist of ferric hydrate and basic arsenate of iron.

Shot metal is an alloy of lead and arsenic.

REACTIONS OF ARSENIC

Dry Reactions.—On charcoal alone, or mixed with fusion mixture in the reducing flame, arsenic gives an odour of garlic, and a white incrustation on the charcoal volatile in the oxidizing flame.

Heated in an open tube the same result is obtained.

Mixed with fusion mixture, and a little charcoal, and heated in a closed tube, a metallic mirror is obtained as a sublimate on the side of the tube.

Held on an asbestos thread in the reducing flame of the bunsen, the flame is tinged white, and a cold body held in the flame receives a black metallic deposit. On cautiously heating this, or the mirror obtained in the tube, to 200° C., it acquires a silvery lustre.

Wet Reactions—Sulphuretted hydrogen yields, in acid solutions, a yellow precipitate, insoluble in hydrochloric acid but soluble in alkaline sulphides or hydrates, and in ammonium carbonate, from which solutions it is precipitated by hydrochloric acid. This precipitate is therefore not produced in solutions containing a considerable quantity of free caustic soda, but falls on making the solution acid.

Solutions of arsenites, or of white arsenic in soda, give the following reactions :—

Neutralized with very dilute nitric acid, on addition of silver nitrate a yellow precipitate (Ag_3AsO_3) is thrown down, soluble in acids or caustic soda.

Neutralized, and ammoniacal copper sulphate added, a green precipitate is thrown down (Scheele's green), CuHAsO_2 .

Arsenates :—Neutral solutions of arsenates turn yellow when saturated with sulphuretted hydrogen, but seldom yield a precipitate. On acidifying with hydrochloric acid, and boiling, a yellow precipitate of As_2S_5 and sulphur falls.

After reduction with hydrochloric acid and sodium sulphite, As_2S_3 is precipitated without difficulty.

Silver nitrate in neutral solution produces a brick-red precipitate.

Copper sulphate in neutral solutions yields a white precipitate.

Magnesia mixture, added to solutions made strongly alkaline with ammonia, gives, on vigorous shaking, a white crystalline precipitate ($\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$).

Ammonium molybdate in nitric acid solution yields, on warming, a yellow crystalline precipitate.

When ferric chloride is added to a solution containing arsenic as arsenic acid, and then ammonia in excess, or if after the addition of ferric chloride sodium or ammonium acetate be added, and the solution boiled, the precipitate which falls contains the whole of the arsenic, as basic ferric arsenate. Arsenic may also be removed from solution, as lead arsenate by addition of lead nitrate and ammonium carbonate in excess.

Reinsch's Test.—On boiling a solution containing arsenic with HCl and clean strips of copper, the arsenic deposits as a grey metallic film on the copper. On heating the strips in a closed tube, the arsenic volatilizes and deposits on the tube. On heating the strips in an open tube (Fig. 81), the As is oxidized to As_2O_3 , which deposits on the side of the tube. The sublimate may be dissolved and tested after neutralization with copper sulphate.

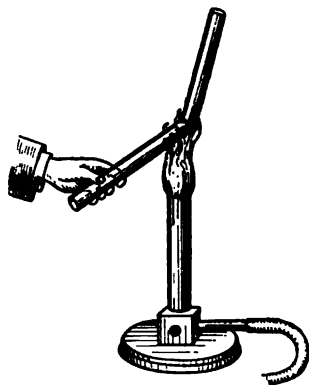


FIG. 81.

Marsh's Test.—If substances containing arsenic be put into an apparatus evolving hydrogen, the arsenic is given off as arseniuretted hydrogen, AsH_3 . When this gas is burnt, it gives the characteristic

bluish-white flame and odour, and deposits a mirror of arsenic on a cold body held in the flame. This method is largely employed in testing soluble materials for arsenic.

Fit up an ordinary hydrogen generating apparatus with a flask holding about 300 c.c., a safety funnel, and a drying tube, through

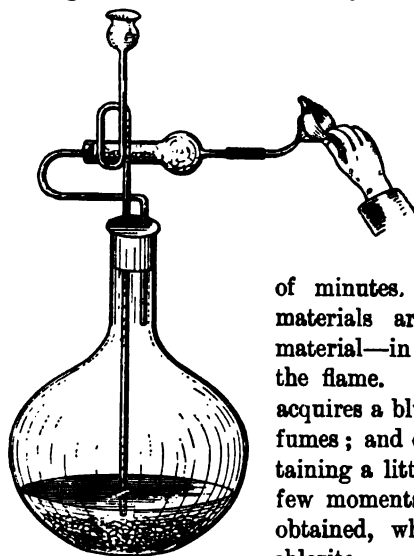


FIG. 82.

which the gas is led (Fig. 82). Charge it with pure zinc (preferably granulated), and pure dilute hydrochloric acid, free from arsenic. When the air is expelled, attach a glass jet to the delivery tube and ignite the dry gas. Hold a cold porcelain dish over the flame for a couple

of minutes. If no stain is produced the materials are pure. Add the suspected material—in solution, if possible—and watch the flame. If much arsenic be present it acquires a bluish tinge, and also gives white fumes; and on holding a porcelain dish, containing a little cold water, in the flame for a few moments an arsenical mirror deposit is obtained, which is soluble in sodium hypochlorite.

Another and safer method is to lead the dry gas through a capillary hard glass tube heated to redness. The AsH_3 is decomposed, and arsenic is deposited as a mirror on the side of the tube.

Antimonial compounds yield deposits which resemble those of arsenic, but are insoluble in sodium hypochlorite.

Arseniuretted hydrogen being highly poisonous, these tests should be carried out in a good draught chamber, and the hydrogen flame should not be allowed to go out after the addition of the arsenical substance or solution.

DRY ASSAY.

(1) **Metallic Arsenic.**—Native arsenic, mispickel, and leucopyrite are assayed by heating with charcoal and sodium carbonate. The available arsenic volatilizes, and is recovered by condensation. With mispickel the reaction is $\text{FeAsS} = \text{FeS} + \text{As}$ and with leucopyrite $\text{Fe}_2\text{As}_2 = 2\text{FeAs} + \text{As}$. Native arsenic sublimes, and any arsenious oxide present is reduced and the arsenic evolved.

From 100 to 500 grms. of material is mixed with one-fifth its weight of charcoal and its own weight of sodium carbonate. The mixture is put into a tubular retort, closed at one end, which it should about half fill. A strip of iron, 5 to 6 inches wide, is loosely coiled into a spiral and placed in the open end of the tube, which is closed by a sheet metal cap, loosely luted to allow of the escape of gases generated. The end of the tube containing the charge is put into the furnace, with the end containing the spiral projecting, and is heated to full redness for about an hour, or longer if necessary.

After cooling, the tube is removed, the sheet-iron spiral taken out and unrolled over a sheet of glazed paper. The arsenic, which is in bright flakes, or as a loosely agglomerated powder, is detached from the iron, and any adhering to the cap or on the sides of the tube added, and the whole is weighed. Scales are formed when the end of the tube containing the spiral gets hot, either by overheating or by the smallness of the condenser; powder is produced when the condenser is large and cool.

(2) **White Arsenic.**—The ore is heated in a current of air and the As_2O_3 collected.

Five to 10 grms. of ore is placed near the open end of a glass combustion tube, the other end of which is drawn out into a narrow tube and bent at a slightly obtuse angle. The tube is placed in a combustion furnace, with the bent end inclining slightly downwards. This end passes into one neck of a large Woulff's bottle, which is connected by the other with an aspirator. The aspirator is set going, the ore is heated, and the arsenious oxide formed passes over into the cool end of the tube and the Woulff's bottle. By careful heating it is driven to the bent part of the tube, which is cut off.

The white arsenic obtained may be weighed, but is better determined by one of the following methods.

WET METHODS

These give the total arsenic.

Estimation as Lead Arsenate.—From 1 to 3 grms. of the ore is mixed with four times its weight of nitre, and 2 to 4 times its weight of sodium carbonate. This is put into a porcelain crucible, covered with a layer of the fluxes, and fused for 10 minutes. The deflagrated mass is boiled with water, and the insoluble residue filtered off and washed. The solution is carefully acidified with nitric acid, and evaporated to dryness to render silica insoluble. The dry mass is treated with water and dilute nitric acid, and the residue filtered and well washed. To the solution 3–6.5 grms. lead nitrate in solution is added.

By this means the sulphates (produced in the fusion) are precipitated as lead sulphate, whilst lead arsenate, being soluble in nitric acid, remains in solution. After filtering off the precipitated lead sulphate the lead arsenate is thrown down by cautiously neutralizing the solution with caustic soda or ammonia. The precipitated arsenate of lead is filtered off on a tared paper, washed, dried, and weighed. The precipitate contains 17.83 per cent. of arsenic.

Another method of getting the arsenic into solution is to digest the ore in nitric acid with additions of potassium chlorate in small quantities at a time. When all action is finished the solution may be diluted, lead nitrate added, and dealt with as before.

- **Estimation of Arsenic as Magnesium Pyroarsenate.**—The solution in nitric acid (obtained as above), after filtering off the insoluble silica, is made strongly alkaline with caustic soda, sulphuretted hydrogen passed to saturation, and the precipitate is filtered off and washed. This precipitate consists of lead, copper, and bismuth sulphides. The filtrate is cautiously acidified with hydrochloric acid, and placed aside in a warm place to allow the arsenious sulphide to settle. The clear liquor is decanted through a filter and the precipitate washed twice by decantation. Any residue on the paper is washed back into the beaker, and the precipitate digested with a strong solution of ammonium carbonate. The insoluble residue is filtered off and the solution acidified with hydrochloric acid, warmed, sulphuretted hydrogen passed to saturation, and let stand for some time.

The precipitated arsenious sulphide is filtered, the precipitate washed back into the beaker, 10 c.c. of nitric acid added, and evaporated to small bulk. The arsenic passes into solution as arsenic acid. Any sulphur that separates is filtered off and washed.

The filtrate is then evaporated to about 50 to 75 c.c.—25 c.c. of strong ammonia added, and 25 c.c. of "magnesia mixture." The solution is vigorously stirred, and allowed to stand for 24 hours. The precipitate is filtered off, and the filtrate collected and measured. The precipitate is well washed with small quantities of dilute ammonia, first by decantation and finally on the filter, dried at 120° C., and carefully detached from the filter paper, which is carefully but completely burnt in a porcelain crucible. The ash is wetted with strong nitric acid and carefully evaporated to dryness. The bulk of the precipitate is then added and heated, gently at first, and finally strongly by means of a blow-pipe or in the muffle. The arsenic remains as pyro arsenate of magnesium, $Mg_2As_2O_7$, and contains 48.416 per cent. of arsenic. On account of its slight solubility an addition of 0.001 grm. is made to the weight of the precipitate for each 16 c.c. of the original filtrate.

Unless the filter paper is carefully burnt, some loss of arsenic is certain to occur. The quantity lost depends on the completeness with which the precipitate is removed prior to ignition.

It is better, although somewhat more tedious, to collect the precipitate on a tared paper, previously dried at 100° C., dry in the water bath and reweigh. The precipitate thus treated yields $\text{MgNH}_4\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, which contains 0.3947 of its weight or 39.47 per cent. of arsenic.

Estimation of Arsenic by Treatment with Chlorine Gas (Parnell's Method).—The sample, weighing from 2 to 5 grms., in a porcelain boat is placed in a glass tube and heated to about 200° C., a gentle stream of chlorine being passed through the tube. The arsenic chloride produced being volatile, is collected in a flask containing chlorine water.

Sulphurous acid is added in slight excess, and the arsenic precipitated in the hot solution by sulphuretted hydrogen as arsenic trisulphide mixed with sulphur. The precipitate is collected on a tared filter, washed with water, then with alcohol (to remove water), then with carbon disulphide to remove sulphur, dried in a water bath, and weighed. The precipitate contains 60.959 per cent. of arsenic.

When antimony is present its separation must be effected by dissolving the precipitate and proceeding as directed above.

VOLUMETRIC DETERMINATION.

Estimation of Arsenic by Titration with Iodine.—Iodine added to solution of sodium arsenite, or arsenious acid dissolved in soda, oxidizes it to arsenic acid, thus :—



Standard Solution of Iodine.—2.5 grms. of iodine and 4 grms. of potassium iodide are weighed out and dissolved in water without heat. The solution is made up to 500 c.c.

Standard Solution of Arsenious Acid.—4.95 grms. of white arsenic (pure) are treated with 20 grms. of sodium bicarbonate and water. The solution is poured off into a litre flask, and the treatment repeated till the arsenic is dissolved. When solution is complete, 20 grms. more bicarbonate is added, and the flask filled to the mark.

Starch Solution.—0.5 gm. of starch is ground with water and added to about 300 c.c. of boiling water.

Standardizing the Iodine Solution.—10 c.c. of the arsenic solution is put into a flask, a little bicarbonate of soda added, and diluted to 100 c.c. Starch solution is added, and the iodine solution run in from a burette till a permanent blue colour is produced. This must not

disappear on standing or on the addition of sodium bicarbonate. The value of the iodine solution is then calculated.

Assay of Ores.—The ore is treated as described on p. 249. The tube containing the white arsenic and the Woulff's bottle are washed out several times with a strong solution of sodium bicarbonate. The liquid is made up to 250 or 500 c.c., according to the amount of deposit, 50 to 100 c.c. of the solution taken, and titrated as above.

In dealing with arsenates, they must first be reduced in acid solution by means of sulphur dioxide or sodium sulphite, the solution boiled to expel the excess of sulphur dioxide, and sodium bicarbonate added in excess. Care must be taken to completely decompose the sulphite of soda and to expel sulphur dioxide. The solution is then titrated with iodine.

ANTIMONY.

THE substances in which the determination of this metal is generally required are—

(1) Ores.

Stibnite, antimonite, Sb_2S_3 .
Antimony ochre, and cervantite.
Kermesite, $2\text{Sb}_2\text{O}_3\text{Sb}_2\text{S}_3$.
Valentinite, Sb_2O_3 .
Senarmontite, Sb_2O_3 .
Jamiesonite, $3\text{PbS}_2\text{Sb}_2\text{S}_3$.
Boulangerite, $3\text{PbS Sb}_2\text{S}_3$.

(2) Drosses from softening of lead, etc.

(3) Fume.

(4) Alloys.

Stibnite is a heavy grey mineral which occurs both massive and crystallized. The crystals are long needle-shaped rhombic prisms, "needle ore," and have a most brilliant, almost silvery, metallic lustre. The cleavage is very perfect. When massive traces of crystalline structure are often present and the colour is darker. It is extremely brittle. Hardness, 2. Sp. gr., 4.6–4.7. Sectile. Very fusible. The mineral is soluble in hot hydrochloric acid, sulphuretted hydrogen being evolved.

Antimony ochre is a white or yellowish earthy or granular mineral, which gives the usual blow-pipe reactions for antimony. It is an oxide, or mixture of oxides, and is associated with and often mixed with stibnite.

Kermesite is a red or reddish mineral. Its crystals are monoclinic. It is somewhat softer than stibnite, but behaves in the same manner before the blow-pipe. The crystals are needle-shaped.

Valentinite is the rhombic form of Sb_2O_3 . It is generally white, but sometimes tinted. Volatilizes when heated in a closed tube and on charcoal, first becoming yellow; is readily fusible, and gives the antimony reactions.

Senarmontite is the cubic form of Sb_2O_3 , and behaves like valentinite. The crystals are regular octahedra.

Jamiesonite and **Boulangerite** are heavy lead grey minerals, consisting of antimony and lead sulphides. The former sometimes resembles antimonite, but the crystals are less brilliant, and the cleavage less perfect. It fuses easily, but decrepitates on heating. Before the blow-pipe it behaves like antimonite, but the bead is less brittle. **Steinmannite**, **zinkenite**, **plagionite**, and **plumosite** are other mixtures of lead and antimony sulphides which occur more rarely.

The **drosses** from the softening of lead contain much litharge, and often iron and tin in addition to oxide of antimony. They may be fused or pulverulent.

The **alloys** into which antimony largely enters are type and stereotype metal, white anti-friction alloys, pewter and other hardened lead alloys, for analysis of which, see Part III.

REACTIONS OF ANTIMONY.

Dry Reactions.—Heated on charcoal before the blow-pipe the metal fuses readily, and in oxidizing flame oxidizes freely. It gives a white incrustation on charcoal, which is volatile in R.F., is faintly yellow while hot, but does not give a green coloration on moistening with cobalt nitrate and reheating (distinction from zinc).

Compounds of antimony mixed with fusion mixture ($\text{KCN}, \text{Na}_2\text{CO}_3$) yield brittle beads of antimony with a white incrustation when heated before the blow-pipe.

The sulphide and trioxide volatilize when strongly heated.

Heated on a thread of asbestos in the R.F. of bunsen, antimony compounds colour the flame greenish-white. If a cold porcelain basin be held over the flame, a black lustrous deposit of metallic antimony is produced, which is insoluble in sodium hypochlorite.

Wet Tests.—The metal is soluble in concentrated hydrochloric acid, and in aqua regia yielding SbCl_3 and SbCl_5 , respectively, but nitric acid converts it into a white insoluble hydrate of Sb_2O_5 . Strong sulphuric acid, when heated, dissolves the metal forming the sulphate.

Antimony compounds in solution behave, to a certain extent, like bismuth compounds. Strong solutions containing little free acid are precipitated by water, *e.g.* $\text{SbCl}_3 + \text{H}_2\text{O} = \text{SbOCl} + 2\text{HCl}$, but large excess of acid prevents this precipitation. The precipitate is soluble in tartaric acid, and its presence prevents the formation of a precipitate (distinction from bismuth).

1. Treat a few small grains of antimony with nitric acid alone, and repeat with an addition of tartaric acid. In the latter case no white insoluble body remains. Solutions of antimony compounds behave as follows :—

2. The solution acidified with hydrochloric acid, and a brisk current of sulphuretted hydrogen passed, bright orange red Sb_2S_3 falls, readily soluble in caustic soda, or ammonium sulphide, and in hot strong hydrochloric acid. Acids added to the solutions in alkalies reprecipitate the sulphide.

3. Sodium hydrate added to the solution throws down a white precipitate (Sb_2O_3) soluble in excess.

4. Ammonia produces the same precipitate, but excess of the reagent does not redissolve it.

5. Zinc added to the solution precipitates the antimony.

6. If a piece of platinum foil be placed in the solution and a rod of zinc placed on it, the foil will be coated with a black film of antimony.

7. Antimony gives by Marsh's test a mirror like that of arsenic, but the film is insoluble in sodium hypochlorite.

In applying the tests to a mineral it may be digested with hydrochloric acid and the excess of acid neutralized by soda. As most antimonial minerals contain other metals which give precipitates with sulphuretted hydrogen, it is better to proceed as follows. The solution obtained by digesting with hydrochloric acid, or aqua regia, is made alkaline with caustic soda, saturated with sulphuretted hydrogen and allowed to stand. The residue and precipitate are then filtered off, and the solution acidified with hydrochloric acid. A red precipitate of Sb_2S_3 falls. The precipitate must be dissolved in hydrochloric acid and the solution further tested, as above.

DRY ASSAY OF ANTIMONY.

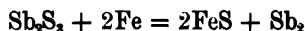
This may take one of two forms. In some cases the determination of antimony sulphide in the ore—crude antimony—is required. In most cases, however, the determination of the metal—regulus of antimony—is made.

Liquation Assay of Antimony Sulphide.—The determination of the quantity of antimony sulphide contained in an ore depends on the ready fusibility of the sulphide. It is conducted as follows :—

Two pots are selected, one of which fits into the other to about half its depth. The bottom of the upper one is perforated with $\frac{1}{4}$ -inch holes. The joint is well luted with sand and fireclay lute. Half a

pound or 500 grms. of roughly broken ore—as large as small peas—not powdered, is put into the upper crucible and the cover well luted. The whole is dried. The pots are put into a cold furnace, and the bottom filled with broken fire-bricks half-way up the crucibles. On these the fire is made so that the upper pot only is heated. Or, the bottom of the lower pot may project below the fire bars to keep it cool. The temperature should not exceed dull redness, and is maintained for an hour or more. The sulphide in the ore fuses and collects in the lower crucible. The pots are taken out, allowed to cool, separated, and the sulphide carefully melted, poured into a mould, and weighed.

Assay of Antimony Sulphide by Iron and Black Flux.—Owing to the volatile character of the metal, the difficulty of decomposing its compounds and the simultaneous reduction of other metals, from which it is difficult to purify it, the dry assay of antimony does not yield accurate results; but in this, as in some other cases, dealings in ores are transacted on the results obtained by dry assay. This method of assay is attended with difficulty, owing to the combination of the reduced antimony with any excess of iron, which thus increases the weight of the button, and also antimony may pass as antimoniate into the slag. The quantity of iron used must be always less than is actually required to precipitate the antimony.



The charge is made up of—

20 grms. ore.

30 grms. potassium carbonate and flour. See Black Flux.

8 grms. iron filings.

6 grms. borax glass.

The mixture is put into a crucible, and carefully heated for 30 to 45 minutes, finishing at a full red heat. This must not, however, be maintained for any considerable time, but the assay poured into a mould as soon as the reaction is complete, otherwise excessive loss by volatilization will occur. The metal is separated from the slag by washing and gentle tapping. If the assay has been properly conducted, the button will be round and well formed, with a bluish-white colour and crystalline surface. The metal will be brittle, and the fracture will present broad clear, bright facets. Foreign metals, especially iron, cause the fracture to be less crystalline, and the facets dull or spotted when examined with a lens.

The loss by this method on fairly pure sulphides is about 4 per cent. It answers for mixtures of sulphide with oxides, but the quantity of iron must be adjusted.

Sodium sulphate, 20 grms., and charcoal, 2 grms., are sometimes substituted for the black flux substitute, but the loss is generally greater, and may reach 10 per cent.

The button of metal obtained in this and other dry assays may contain iron, copper, lead, and other metals. In such cases the antimony may be determined by pounding the button, and treating it with strong nitric acid. When the action is complete, the liquor is diluted with water, boiled and the Sb_2O_3 produced, filtered off, washed, dried, ignited in a porcelain crucible, and weighed. The weight multiplied by 0.7926 gives the metallic antimony. Where the latter practice is followed, the charge of antimony sulphide should not exceed 5 grms., and other substances in proportion.

Assay of Antimony Sulphide by Potassium Cyanide.—The charge consists of—

- 10 grms. ore.
- 40 „ potassium cyanide.
- Salt cover.

Some of the cyanide, say 10 grms., is put as a layer at the bottom of the crucible. The ore is mixed with the remainder, and placed on this, and the whole covered with a layer of dry salt. The crucible is carefully heated to full fusion of the charge, and kept at this temperature for 15 to 20 minutes, and the assay poured into a mould. The button is detached, and, after cleaning, weighed.

Some assayers substitute potassium ferrocyanide for the greater part of the cyanide thus: 10 grms. of ore are mixed with 20 of anhydrous potassium ferrocyanide, and put into a crucible on a layer of the same substance. This is covered with 5 to 10 grms. of potassium cyanide and a salt cover. The operation is conducted as before.

Assay of Oxidized Ores of Antimony.—This is a simple case of reduction. The charge is :—

- (a) 20 grms. ore.
- 50 „ black flux substitute (potassium carbonate and flour).
- Salt cover.
- (b) 20 grms. ore.
- 20 „ sodium carbonate.
- 10 to 20 grms. argol.
- Salt cover.

The fusion is conducted with the same precautions as for sulphide assays.

(c) The cyanide assay as detailed for sulphide ores is equally applicable to oxides, and is preferred by many.

Assay of Sulphide of Antimony by Roasting and Reduction.—This method of assaying antimony sulphide has little to recommend it, and is very

tedious. The sulphide is converted into oxide by carefully roasting it at a low heat till only yellowish-white Sb_2O_3 remains. It is then treated as an oxidized ore, or melted with twice its weight of black flux substitute, its own weight of sodium carbonate, and its own weight of argol.

At the smelting works the ore is assayed by an actual trial conducted on about 2 cwts. of ore.

WET ASSAY OF ANTIMONY.

Determinations of antimony by wet processes are based on (1) the insolubility of the sulphide in dilute hydrochloric acid, and its solubility in alkaline sulphides and caustic alkalis; (2) the formation of an insoluble precipitate with gallic acid; (3) the liberation of iodine from potassium iodide by antimonious chloride, and (4) in the case of metallic bodies the formation of an insoluble oxide on treatment with nitric acid, which is soluble in tartaric acid. The separation from other metals is based on the solubility of the sulphide in ammonium sulphide and caustic alkalis from which it is reprecipitated by acids, the solubility of the sulphide in strong hydrochloric acid and the solubility of the oxide in tartaric acid.

Estimation of Antimony as Sulphide.—From 0.25 to 5 grms. of the finely divided ore is placed in a beaker, covered with strong hydrochloric acid, and warmed till no further action takes place, more acid being added if necessary. The solution is then evaporated to small bulk with nitric acid, saturated with tartaric acid (crystals), and

made strongly alkaline with caustic soda. The liquor is then saturated with sulphuretted hydrogen, and

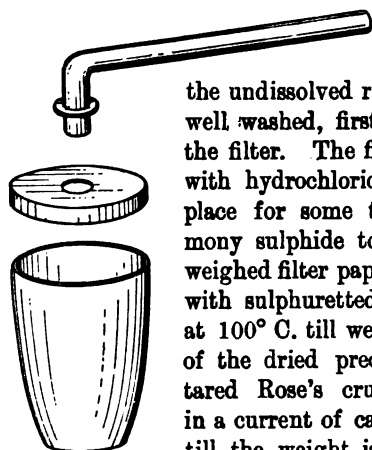


FIG. 83.

the undissolved residue and precipitate filtered off and well washed, first by decantation, and afterwards on the filter. The filtrate and washings are then acidified with hydrochloric acid, and placed aside in a warm place for some time to allow the precipitated antimony sulphide to settle out. This is collected on a weighed filter paper, previously dried at 100°C ., washed with sulphuretted hydrogen water, and after drying at 100°C . till weight is constant, weighed. A portion of the dried precipitate is then weighed, placed in a tared Rose's crucible (Fig. 83), and heated gently in a current of carbon dioxide (to expel free sulphur) till the weight is constant. Or the heating may be done in a porcelain boat, in a piece of combustion-tube (see Fig. 80). The weight of antimony sulphide in the original

precipitate and the percentage in the ore are calculated, and this multiplied by 0.718 gives the percentage of antimony.

<i>Example.</i> —Weight of ore taken	= 0.5	gram.
Weight of precipitate after drying	= 0.416	„
Weight taken for heating	= 0.312	„
Weight after heating in CO ₂	= 0.26	„
Loss of weight	= 0.052	„

Then $\frac{0.26}{0.312} \times 0.416 = 0.346$ (weight of antimony sulphide in the precipitate).

and $\frac{0.346}{0.5} \times 100 = \frac{34.6}{0.5} = 69.2$ per cent. of Sb₂S₃ in the ore.

$69.2 \times 0.718 = 49.585$ per cent. of antimony

There is one difficulty with this method, viz. the removal from the crucible of the antimony sulphide which fuses on heating. This can be done by digestion with hydrochloric acid, a little potassium chlorate being added in small portions at a time.

A quicker and no less accurate method is to redissolve the Sb₂S₃ in hydrochloric acid, and estimate it by one of the following methods.

Estimation of Antimony as Bigallate.—The antimony sulphide separated as in previous method is dissolved by boiling in as little hydrochloric acid as possible. Any sulphur remaining undissolved is filtered off. Potassium iodide is added to the hot solution till no more iodine is liberated,* and the liquor evaporated to dryness on the water bath. By this means the antimony is reduced to antimonious chloride, and the liberated iodine expelled.



The evaporation must be done on a water bath, as antimony chloride is volatile.

The residue is taken up with water, just sufficient hydrochloric acid added to keep the solution clear, i.e. to prevent the precipitation of antimony oxychloride, and a freshly prepared solution of gallic acid added. After standing some time in a warm place to settle, the clear liquor is decanted through a weighed filter dried at 100° C., the precipitate washed once or twice with hot water by decantation, and finally on the filter. It is dried at 100° C., and weighed. It contains 40.85 per cent. of Sb.

Assay of Antimony Sulphide.—Finely powder the antimony sulphide and pass through an 80 sieve. Mix 1 gram. of the sample with a little milk of sulphur, and digest with 20 c.c. potassium sulphide.

* If iodine be liberated the solution will become brown.

Filter off the insoluble matter (copper, iron, and lead sulphides). Dilute to 100 c.c. with water, and saturate with sulphurous acid gas. Warm 15 minutes, and then evaporate to one-third its bulk, till SO_2 is expelled. Let settle. Filter off precipitated Sb_2S_3 , wash with water, then with alcohol, and finally with carbon disulphide, dry at 100°C ., and weigh. Or, transfer to a weighed crucible, and treat cautiously with fuming nitric acid till converted to Sb_2O_4 . Evaporate, ignite, and weigh.

Factor for antimony 0.7926.

VOLUMETRIC ASSAY OF ANTIMONY.

Iodide Method.—The assay of antimony by this method is effected by determining the quantity of iodine liberated by antimonious chloride when treated with potassium iodide according to the reaction given above. The important point of the process is the complete conversion of the antimony into SbCl_3 without leaving any excess of free chlorine.

The determination of the free iodine is carried out much in the same manner as the corresponding method for estimating copper (p. 85), and the same standard solution of thiosulphate may be used. Starch solution will also be required (p. 86).

Standardizing.—The thiosulphate is standardized by weighing out two quantities of 0.5 grm. of antimony, dissolving them in hydrochloric acid and nitric acid (4 parts HCl , 1 HNO_3), taking care that no excess of nitric acid is employed. The solution is evaporated to small bulk to completely expel free chlorine, hydrochloric acid added, and the liquid diluted with water to 100 c.c. Potassium iodide equal to four or five times the weight of the antimony present is then added and dissolved, and the titration proceeded with exactly as described for copper. When the reaction is complete the liquid should be clear, and contain no precipitate, as SbCl_3 is soluble in acid solutions.

Analysis.—The precipitated sulphide, separated as described on p. 258, is dissolved in boiling hydrochloric acid with the addition of a little nitric acid or potassium chlorate, and evaporated to small bulk. Sufficient hydrochloric acid must be present to completely decompose the nitric acid or potassium chlorate added, as no trace of free chlorine must remain in the strongly acid liquor. There is no need to filter, and the addition of potassium iodide and after cooling titration with thiosulphate may be proceeded with exactly as before.

Estimation of Antimony in Metal and Alloys.—In alloys containing no tin, the weighed quantity of the alloy may be dissolved in strong

nitric acid, diluted with water, and evaporated to small bulk. The residual hydrated Sb_2O_3 is then filtered off, washed, dried, ignited, and weighed as Sb_2O_3 . From 1-5 grms. of the alloy are taken. The precipitate must be removed from the filter paper, which is burnt alone, and the ash caught on the lid of the porcelain crucible, to which the precipitate has been transferred. It is moistened with nitric acid and evaporated to dryness. The lid is placed on the crucible, and the whole is ignited and weighed. Factor for Sb = 0.7926.

For estimation in alloys containing tin, see p. 299.

BISMUTH.

THE substances in which the determination of the metal is generally required, are—

Ores { Native bismuth, Bi.
Bismuthine, Bi_2S_3 .
Agnesite, Bi_2O_3 .

Metallic bismuth.

Lead.

Fusible alloys.

Cupel bottoms.

Litharge.

Ores of Bismuth.—Native bismuth occurs sometimes crystallized, but more commonly in lamellar or granular masses. It has a white metallic lustre, with a pinkish tinge, sometimes yellowish or tarnished. Hardness, 2·5; sp. gr., 9·6 to 9·8. Very brittle. Fuses readily on charcoal, and in R.F. volatilizes, giving an orange-yellow coating. It generally occurs associated with nickel, arsenic, cobalt, nickel, and lead minerals.

Bismuthine.—Sulphide of bismuth, Bi_2S_3 , occurs in prismatic crystals, often very delicate and strongly striated, also granular and massive. Colour, light lead grey with yellowish coloured tarnish. Hardness, 2 to 2·5; sp. gr., 6·4 to 6·6. Sectile and brittle. Before blowpipe, fuses and yields a metallic bead with yellow incrustation. Soluble in nitric acid.

Bismuth Ochre, Agnesite, is an earthy mineral of a white, yellow, or greyish yellow colour. Fuses on charcoal and yields a bead of bismuth.

Bismuthite.—The carbonate occurs as an earthy white to yellow mineral. It is imported from Mexico and other countries.

Cupreous bismuth, CuBiS_2 , Tetradymite, $2\text{Bi}_2\text{Te}_3\text{Bi}_2\text{S}_3$, also occur.

Ores of other metals often contain bismuth. It often occurs in lead and in litharge.

Bismuthic litharge is greenish black in colour.

The following table shows the composition of the more common fusible alloys :—

		Newton's.	Rose's.	Lechtanberg's metal.	Wood's.
Bismuth	...	8	2	5	4
Lead	...	5	1	3	2
Tin	...	3	1	2	1
Cadmium	...	—	—	—	1
Melting points	...	94°·5	93°·75	91°·6	60°·5 C.

REACTIONS OF BISMUTH.

The metal is readily soluble in nitric and hot strong sulphuric acids, but is only difficultly soluble in hydrochloric acid ; it is readily fusible.

Dry Tests.—Heated on charcoal with fusion mixture bismuth compounds yield a bead of metallic bismuth, with a yellow or orange incrustation on the charcoal.

Wet Tests.—Most of the salts of bismuth in solution are decomposed when water is added, a basic salt being precipitated. Hence a little free acid is always necessary to keep the solutions clear. All bismuth compounds are soluble in acids.

1. Sulphuretted hydrogen in hydrochloric acid solution precipitates bismuth sulphide, Bi_2S_3 , insoluble in cold dilute acids, ammonium sulphide, or sodium hydrate, soluble in boiling nitric acid.

NOTE.—In acidifying with hydrochloric acid, a white precipitate of bismuth oxychloride, BiOCl , may be thrown down, which dissolves on the addition of more acid.

2. Ammonia precipitates white bismuth hydrate, $\text{Bi}_2(\text{HO})_6$, insoluble in excess.

3. Sodium hydrate produces the same precipitate, insoluble in excess.

4. Sodium carbonate throws down a basic carbonate of uncertain composition.

5. Potassium chromate gives a yellow precipitate of bismuth chromate, $\text{Bi}_2(\text{CrO}_4)_3$, insoluble in caustic soda (compare Lead), soluble in nitric acid.

6. Strong solutions of bismuth salts when added to a large quantity of water give white precipitates of basic salts. The oxychloride is insoluble in tartaric acid (distinction from antimony).

7. Caustic soda added to a solution of bismuth chloride, containing stannous chloride and tartaric acid, gives, on warming, a grey streaky or nearly black precipitate (magpie test). One part of bismuth in about

200,000 of the solution may be detected in this way. Mercury, copper, and manganese interfere with this test. "Schneider's" liquid for the detection of bismuth is made by dissolving 12 grms. of tartaric acid, 4 grms. of stannous chloride, in water, and adding potash till alkaline.

8. Iron, copper, lead, zinc, and tin precipitate metallic bismuth.

9. Potassium iodide gives a precipitate of bismuth iodide which dissolves in excess, yielding a brown solution undistinguishable from free iodine. It is not decolorized by boiling.

DRY ASSAY OF BISMUTH.

Owing to the ready volatility of the metal only very approximate results can be obtained. With impure ores foreign metals are also reduced.

Assay of Ores and Compounds Free from Sulphur.—5 to 15 grms. of the ore is mixed with two and a half times its weight of white flux (see p. 35), and about 3 grms. of borax. The charge is introduced into a crucible, covered with salt, and heated gently till flaming ceases. The temperature is then raised to full redness (not too bright), and the assay fused for 20 to 25 minutes. When quietly fused, the assay is poured into a mould, or allowed to cool, and broken out.

Potassium cyanide is frequently used as the reducing agent. The ore is then mixed with its own weight of carbonate of soda and of potassium cyanide, and a little borax added. The assay is covered with salt, and melted at a cherry-red heat. Lead, tin, copper, and antimony pass into the metal.

Another flux consists of 2 parts sodium carbonate, and 1 part salt, with argol or potassium cyanide as a reducing agent.

A flux for bismuth must yield an extremely fusible slag, so that high temperatures may be avoided.

Assay of Sulphurized Ores (Free, or nearly free from Copper).—The ore is placed in an iron crucible, or in a clay crucible, in which two or three thick bent iron wires are placed vertically. The ore is covered with two to three times its weight of white flux, one-third of its weight of borax, and some salt, and heated as before.

It is, however, much better to roast bismuth sulphide to oxide before assaying. If arsenic be present, the crucible or dish should be covered till this element is expelled, or arsenates will be formed and remain. Antimony is partly eliminated in roasting. All lead and antimony remaining in the ore are reduced.

Assay of Ores with Copper present (Tamm's Process).—This

process is based on the fact that bismuth sulphide is reduced by carbon, while copper sulphide is not.

Oxidized ores are heated with a flux, consisting of

- 5 parts potassium carbonate or sodium carbonate.
- 2 „ salt.
- 2 „ sulphur.
- 1 „ charcoal.

The ore is fused with its own weight of the above flux. The copper remains in the slag as sulphide. Arsenic and antimony also pass mainly into the slag, unless present in large quantity. Metallic iron must be excluded, or copper will be reduced, and sufficient sulphur must be present to completely sulphurize both iron and copper. The loss of bismuth is about 8 per cent. of the metal present.

Refining.—The crude metal often contains Pb, As, Sb, Cu, Te. To some extent the amount of impurity may be judged by the fracture.

Arsenical bismuth is more brittle and whiter, and the laminæ are larger. Cupreous bismuth often exhibits distinct traces of copper on the facets. Antimonial bismuth is duller, and the fracture is less largely crystalline. Telluric bismuth is whiter, and the fracture is much more finely crystalline. Lead (in small quantities) does not interfere with its crystallization, but the large facets are often covered with little crystals.

Arsenic is tested for before the blowpipe, the garlic odour is perceptible even with traces of the element.

Copper is detected by the ammonia test; antimony by treating the metal with strong nitric acid, white oxide of antimony remaining if antimony be present. Tellurium may be detected in faintly acid solution by the sodium sulphite test. Lead is tested for by dissolving the metal in strong nitric acid and boiling off the excess acid with hydrochloric acid. The solution is treated with ammonia in excess, the precipitate redissolved in the minimum amount of hydrochloric acid, and pure sodium sulphate added; any cloudiness is due to the presence of lead, providing the solution is faintly acid. Or, the hydrochloric acid solution (1 : 1) is treated with boiling water to precipitate the Bi, the liquid filtered, and ammonia and ammonium carbonate added in excess. If lead be present, a yellowish white precipitate is formed.

Copper is removed in Tamm's process by fusion under sulphocyanide of potassium, or by heating at a dull heat with potassium cyanide and sulphur, a clay stirrer being used. Sulphur is subsequently removed by stirring with an iron rod, when removing arsenic. Lead is partly removed in the various refinings, which should be conducted in

the order given. Some lead always remains. This does not affect the appearance of the bismuth.

Antimony is removed by scorification, by fusion with oxide of bismuth, or by treating with nitre.

Arsenic is removed by heating with iron under a flux of sodium carbonate and borax. The bismuth takes up practically no iron.

Tellurium may be removed by treatment with caustic soda or by fusion with a flux, consisting of carbonate of soda and carbon in the proportion of 9 parts of carbonate and 1 of carbon. Fusion with sodium carbonate and nitre removes tellurium, but oxidizes the bismuth also.

In dealing with substances by wet processes, in which the bismuth is first precipitated as oxychloride, any tellurium present is largely, and in some cases completely, precipitated as oxychloride, and thus finds its way into the metal.

WET ASSAY OF BISMUTH.

Gravimetric Methods.—Estimation as oxide.

2 to 5 grms. of the ore is dissolved in nitric acid and the solution carefully evaporated. The residue is moistened with sulphuric acid, well stirred, and again evaporated till white fumes come off. When cold, water is added to dissolve the mass (no turbidity should result); any lead is left as insoluble sulphate. The liquid is filtered. The bismuth is then precipitated in the filtrate by ammonium carbonate, filtered, washed, dried, and removed as completely as possible from the paper, which is burnt separately, and the ash moistened with nitric acid, and evaporated to dryness. The precipitate is then added, strongly ignited, and weighed as Bi_2O_3 , which contains 89.767 per cent. of Bi.

This method is not accurate in the presence of hydrochloric acid, as the precipitate contains oxychloride of bismuth, which is partially volatile, and would leave a residue of uncertain composition. When hydrochloric acid is present it is necessary to precipitate the bismuth as sulphide (see below).

In presence of other metals the bismuth must be first precipitated as sulphide, and the precipitate digested with ammonium sulphide, etc., as in ordinary separations (see pp. 267 and 306).

Estimation as Metal.—Lead and bismuth are separated by precipitating the bismuth from a faintly acid solution with lead. The bismuth precipitated by the lead is removed, washed in alcohol, dried, and weighed.

Ullgreen precipitates the bismuth on lead in acetic acid solution,

prepared by first precipitating with ammonium carbonate and dissolving the precipitate in acetic acid. The metal is converted into oxide by treatment with nitric acid, evaporating to dryness, and heating.

Estimation by Precipitation as Sulphide.—The solution in nitric acid is evaporated nearly to dryness with sulphuric acid, as above, the solution after cooling diluted to 100 c.c., heated, and saturated with sulphuretted hydrogen. The precipitate is warmed with ammonium sulphide to remove antimony and tin, filtered, washed, and dried. It is then heated in a closed crucible for about ten minutes, and finally in an open crucible till oxidized. Or the oxidation may be effected by moistening the dry precipitate with nitric acid and cautiously adding fuming nitric acid, sp. gr., 1.5, and heating. This method is only applicable if copper be absent. Or the sulphide may be dissolved by nitric acid, any residue filtered off, and the solution precipitated with ammonium carbonate, as above.

Antimonial and Arsenical Ores.—These may be fused with a mixture of sodium carbonate and sulphur for some time, and the mass extracted with water. Bismuth, lead, copper, iron, remain in the insoluble residue, while antimony, arsenic, and tin pass into solution. The residue is dissolved in acid, excess of acid removed by evaporation, and the solution saturated with sulphuretted hydrogen; the precipitate, after washing, is dissolved in boiling dilute nitric acid, and the solution evaporated to dryness. The residue is moistened with sulphuric acid and bismuth determined as before.

The **Electrolytic assay** of Bismuth is unsatisfactory in the presence of other metals. In the electrolytic assay of copper, bismuth, if present, comes down at the end of the deposition and darkens the deposit. It must be removed by ammonium carbonate prior to electrolysis.

The **volumetric estimation** of bismuth (Muir's method) is conducted as follows :—

Separation of the bismuth as oxalate in weak nitric acid solution (hydrochloric acid must be absent), and repeated boiling of the precipitate with water, yields the basic oxalate ($\text{Bi}_2\text{O}_3 \cdot 2\text{C}_2\text{O}_3 + \text{water}$). This precipitate settles quickly, and is washed by decantation, any passing on to the filter being washed back into the beaker. When the washings cease to show an acid reaction, the precipitate is dissolved in dilute sulphuric acid, and titrated with standard permanganate. Any free hydrochloric acid must be got rid of before precipitation and titration. See Zinc. 2 molecules oxalic acid = 1 molecule Bi_2O_3 . In this, as in other volumetric methods, other metals must be absent.

Bismuth is also estimated by potassium dichromate in nitric acid solution, using silver nitrate as an indicator on a spot plate.

Detection of Bismuth in Copper (Abel and Field's Method).—5 to 10 grms. of the copper is dissolved in nitric acid, and a solution of lead nitrate equal to 0.5 gm. of the salt added. Ammonia and ammonium carbonate are then added in excess, the precipitate collected, washed with weak ammonia, dissolved in hot acetic acid, and an excess of potassium iodide added. The precipitate which falls is darker coloured when bismuth is present than in its absence, and if the liquid be heated till the precipitate dissolves on cooling, the scales of lead iodide deposited are of a darker colour. Thus 0.0002 per cent. gives an orange colour, 0.001 per cent. reddish brown, 0.01 scarlet, like silver chromate.

VANADIUM.

THIS rare metal occurs as—

Vanadinite $3[\text{Pb}_2(\text{VO}_4)_2]\text{PbCl}_2$. Mottramite, a cupro lead vanadate. Dechenite, a vanadate of lead and zinc, and in other rare minerals associated with manganese, bismuth, and other metals. Certain copper and iron ores contain it in minute quantities.

Vanadinite is a brownish yellow mineral, with a resinous lustre, often occurring as scaly, warty masses or nodules. It gives a white streak, and has a hardness of 3, and sp. gr., 6.8 to 7.

Reactions of Vanadium.—**Dry Reactions.**—Vanadium gives, with borax, a bright green colour in the oxidizing flame, which becomes colourless in the reducing flame.

Wet Tests.—Solutions of hypovanadic oxide (V_2O_5) have a blue colour.

Salts of the trioxide V_2O_3 are green, of the dioxide VO_2 , lavender.

Hypovanadic solutions yield with potash a grey-white precipitate, soluble in excess. On further addition the hypovanadate of potash, $\text{K}_2\text{O}(\text{V}_2\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$, is precipitated as a reddish brown precipitate. Ammonia behaves similarly. Ammonium sulphide precipitates the brown sulphide soluble in excess, yielding a brown solution from which the pentasulphide V_2S_5 is precipitated on acidifying. Ammonium chloride precipitates the vanadium as a hydrated vanadate. Gallic acid gives a black solution, which contains a very finely divided precipitate.

Vanadates more or less resemble chromates. They are usually yellow or red, and sparingly soluble in water. On addition of acid they deepen in colour.

Treatment with oxalic acid, sulphur dioxide, or other reducing agent, yields a blue solution—distinction from chromic acid, which turns green.

Sulphuretted hydrogen in ammoniacal solution gives a deep cherry red coloration, from which the sulphide is thrown down on cautiously acidifying.

An ethereal solution of hydrogen peroxide gives a red coloration (vanadic acid).

Lead acetate in neutral or acetic acid solutions gives an intense yellow precipitate of vanadate of lead, insoluble in ammonium carbonate. (Compare Uranium.)

Estimation of Vanadium.—The substance is fused for some time with twice its weight of sodium carbonate and nitre, and carefully extracted with water. The solution is acidified with hydrochloric acid, excess of sulphurous acid added to reduce arsenates, and after boiling off the excess of sulphurous acid, saturated with sulphuretted hydrogen to precipitate the arsenic. After filtering, the sulphuretted hydrogen is boiled off, and the blue liquor is oxidized with chlorine or sodium hypochlorite, neutralized, and barium nitrate added to precipitate the vanadinate. The precipitate of barium vanadinate is digested with dilute sulphuric acid and filtered. The solution is carefully neutralized with ammonia, and ammonium chloride added to saturation. On standing, ammonium vanadinate separates out. It is filtered, washed with dilute ammonia, dried, ignited (cautiously), and weighed as V_2O_5 .

In the absence of Arsenic the process may be curtailed by nearly neutralizing the solution (obtained by extracting the fused mass with water), with nitric acid free from nitrous oxides, filtering off the very slightly alkaline liquor, and precipitating with barium nitrate direct.

Alumina may be separated by dissolving the ammonium vanadinate, reducing with sulphur dioxide in acid solution, nearly neutralizing with ammonia, and adding ammonium sulphide in excess. Alumina, iron, etc., are thrown down while the vanadium goes into solution, and may be separated as sulphide by evaporation after acidifying with hydrochloric acid.

The precipitated alumina may be ignited and its weight deducted from the V_2O_5 .

VOLUMETRIC METHOD.

The process depends on the absorption of oxygen in the conversion of V_2O_4 into V_2O_5 . Potassium permanganate is employed for the purpose of titration. The method is specially applicable for estimating vanadium in iron and steel and alloys.

Two grms. of steel or 0.5 gm. of richer alloys are dissolved in hydrochloric acid with a little strong nitric acid in addition, and evaporated to dryness. The dry residue is fused with twice its weight or more of a mixture of one part nitre, one sodium carbonate, and one part potassium carbonate, for ten minutes. The fused mass, after cooling, is boiled out with water, the solution filtered, and the residue washed. The solution is evaporated nearly to dryness with sulphuric acid. Water is added to 150 c.c., and the liquid saturated with sulphur dioxide, the excess boiled completely off, and the solution titrated with a standard solution of potassium permanganate. In alloys other than iron, the foreign metals must be first precipitated.

MOLYBDENUM.

MOLYBDENUM is met with in nature as molybdenite (sulphide of molybdenum), molybdic ochre, and as wulfenite (molybdate of lead). Other molybdates occasionally occur. Some iron and copper ores also contain molybdenum, which on smelting passes into the slags. It occurs in some self-hardening steels. In practice it is principally used as molybdate of ammonia for analytical purposes, but is also employed as a mordant.

Molybdenite.— MoS_2 is a soft, sectile, lead-grey, metallic solid, closely resembling graphite. It marks paper, soils the hands, and feels unctuous to the touch. The streak is, however, greenish-black, and it gives an odour of SO_2 before the blow-pipe and the molybdenum reactions with borax.

Molybdic Ochre is an earthy, ochreous, yellowish-white or brownish body.

Wulfenite (*see* Lead) is yellow, brownish, or brilliant orange-red in colour, has a waxy lustre, a hardness of about 2·5–3; sp. gr., 6·3–6·9; brittle. It occurs crystallized in tetragonal pyramids and tabular crystals, and also massive. Yields lead before blow-pipe.

Ammonium Molybdate.— $(\text{NH}_4)_2\text{MoO}_4$ (the molybdate of commerce is $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) is the principal molybdenum compound. It is used in the estimation of phosphoric acid (p. 356), lead, and arsenic.

REACTIONS FOR MOLYBDENUM.

Molybdenum forms several oxides— MoO , M_2O_3 , MoO_2 , MoO_3 . The first three are basic, MoO_3 is an acid oxide, whose salts resemble those of chromium. The oxides yield the metal when reduced by hydrogen.

Mo_2O_3 and Mo_3O_8 may be looked upon as $\text{MoO}_2\cdot\text{MoO}_3$ and $\text{MoO}_2\cdot 2\text{MoO}_3$, respectively. They are characteristic blue oxides.

The sulphide on roasting yields MoO_3 , which volatilizes and is deposited as an incrustation. On touching it momentarily with the

R.F. it turns blue. With microcosmic salt yields a yellow bead in the oxidizing flame and a fine green bead in the R.F. With borax the bead is brown and opaque.

The sulphide on treatment with strong nitric acid is converted into MoO_3 . This oxide is soluble in ammonia, yielding ammonium molybdate. It fuses readily, and is volatile. Water dissolves it slightly, but it is soluble in dilute nitric acid and in ammonium nitrate.

Salts of molybdenum yield, on prolonged treatment with sulphuretted hydrogen, a brown black precipitate of MoS_2 or MoS_3 , soluble in ammonium sulphide.

Molybdates.—Sulphuretted hydrogen at first produces a blue solution, but on standing, the dark sulphide is thrown down, and the solution becomes colourless. If the precipitation be incomplete, the solution is green.

Salts of lead precipitate white insoluble molybdate of lead. Soluble phosphates, or phosphates in solution in nitric acid, give, on warming with ammonium molybdate solution, a brilliant canary yellow precipitate of ammonium phosphomolybdate, insoluble in dilute acid, but soluble in alkalis.

DETERMINATION OF MOLYBDENUM.

Gravimetric Methods.—**Method 1.**—The molybdenum in the substance is first converted into molybdic acid, by treating with aqua regia and repeatedly evaporating the solution to small bulk with strong nitric acid till all chlorine is expelled, and then cautiously evaporating to dryness. The residue is extracted with ammonia, filtered, washed, and the filtrate carefully neutralized with nitric or acetic acid. The solution is boiled, and a concentrated neutral solution of lead acetate added in slight excess. On boiling, the milky appearance disappears, the precipitate becomes granular, and settles readily. It is collected on a tared filter dried at 100°C ., and washed thoroughly with hot water. No milkiness should appear in the filtrate. The precipitate PbMoO_4 is dried at 100°C ., and weighed.

Or, the precipitate, after drying, may be detached from the filter paper (it separates well if the paper used is smooth), transferred to a weighed porcelain crucible; the paper burnt and the ash added, and the whole ignited to incipient redness.

Method 2.—Another method of estimating molybdenum is to add to the solution in ammonia, after careful neutralization with nitric acid, an excess of neutral mercurous nitrate solution. The precipitated yellow mercurous molybdate is filtered through a smooth paper washed with

dilute mercurous nitrate solution, and dried at 100°C . It is then detached from the paper, and mixed in a porcelain crucible with a quantity of pure litharge,* previously heated (but not so strongly as to melt), and weighed. The crucible is then ignited over a bunsen, carefully at first, but afterwards strongly, to completely expel mercury, and is finally weighed. The heating and weighing are repeated till the weight is constant. The increase in weight of the litharge = MoO_3 , containing 66.7 per cent. of molybdenum.

Method 3—Molybdic acid may be also estimated by adding a soluble phosphate to the solution (see p. 356).

The yellow precipitate is collected, dissolved in ammonium hydrate or sodium carbonate, the phosphoric acid precipitated with magnesia mixture (see p. 358), and filtered. The filtrate is evaporated to dryness with aqua regia. On treatment with water, the MoO_3 remains undissolved, and may be dissolved in ammonia, and treated as above. Or it may be added to a crucible containing litharge (see above), mixed, and heated. The increase in weight is the molybdic trioxide, which contains 66.7 per cent. of molybdenum.

* The litharge is best made by carefully heating white lead till decomposed.

URANIUM.

URANIUM occurs in nature as pitchblende, uranium ochre, uranite, autunite, johanite, and some rarer minerals.

The oxide and sodium uranate are important compounds. The former is used for staining glass a canary yellow, and the latter as an enamel colour. The nitrate and acetate are used as reagents.

Pitchblende is a heavy, velvety black, hard mineral, with a pitchy lustre. The streak is greenish black. Hardness, 5–6; sp. gr., 6.5–8.

Uranochre is a soft, friable, earthy body of a straw to orange yellow colour.

Uranite is a bright green, micaceous body, often crystallized in square plates. The lustre is pearly. Hardness, 2–2.5. It is a hydrated phosphate of uranium and copper; yields copper before blow-pipe.

Autunite (lime uranite) is a light green to yellow mineral of the same character, but with lime replacing the copper.

Johanite is a hydrated sulphate of uranium.

Pittenerz, which is soft, and has an olive green streak, and Coracite appear to be mixtures, while Liebigite and Voglite, both green, are carbonates with lime and copper respectively.

REACTIONS FOR URANIUM.

Dry Test.—With microcosmic salt uranium gives a greenish yellow bead in the O.F., and a fine green bead in the R.F.

Wet Tests.—Uranous salts are derived from the oxide UO_2 . They yield green solutions. Ammonium sulphide precipitates the black sulphide insoluble in excess. Caustic soda free from carbonate precipitates reddish brown hydrate. Ammonia carbonate precipitates green carbonate soluble in excess.

Uranic salts are derived from UO_2 , UO_3 , and are yellow in colour. Soluble sulphides precipitate the sulphide in absence of alkaline carbonates. Caustic potash in neutral solutions precipitates the yellow.

uranate of potash. Ammonia and caustic soda give similar yellow precipitates insoluble in excess of the precipitant, but soluble in acid.

In the presence of alkaline carbonates, neither ammonium sulphide nor caustic potash precipitate uranium; but in the latter case, on neutralizing the carbonate solution with acid, the uranate of the alkali is precipitated.

Potassium ferrocyanide gives a deep brown precipitate insoluble in hydrochloric acid, decomposed by alkalies.

Uranous salts are converted into uranic salts by oxidizing agents, and the reduction of the uranic salts is effected exactly as with iron. (See p. 173.)

DETERMINATION OF URANIUM.

The finely divided substance is boiled in strong nitric acid and evaporated to dryness. This is repeated if it appears that the decomposition is incomplete. The residue is taken up with hydrochloric acid, diluted, and without filtering saturated with sulphuretted hydrogen while hot, filtered, and the precipitate washed. The filtrate is heated to boiling, peroxidized with nitric acid, neutralized with ammonia, and ammonium carbonate added in excess and boiled. The precipitate contains all foreign metals except zinc. It is filtered and washed. [If bulky it is redissolved in hydrochloric acid and reprecipitated as before.] The filtrate is made acid with hydrochloric acid, ammonia added in considerable excess, boiled for a minute or two, and filtered. The precipitate is washed with ammonium chloride solution, and, finally, once with water. It is dried, ignited, and weighed as $\text{UO}_2\cdot 2\text{UO}_3$, containing 84.938 per cent. uranium.

PLATINUM.

THIS metal occurs in nature in the native state associated with iridium, osmium, rhodium, ruthenium, and palladium. It occurs in alluvial deposits in grains, and in nickel, lead, silver, and gold ores.

Native platinum occurs in flattened rounded grains of a silvery lustre, sometimes crystallized in cubic forms, and occasionally in nuggets. Osmiridium, which is generally found with it, has a hexagonal form, or exists in flat plates. It is extremely hard. Some of the grains are also alloys of iridium and platinum. Small quantities of the other metals are invariably present, while gold, copper, and iron are not infrequent additions.

REACTIONS FOR PLATINUM.

The metal is white and malleable. It is insoluble in nitric acid, but dissolves in aqua regia or other mixtures yielding free chlorine, *e.g.* hydrochloric acid, and potassium chlorate, forming platinic chloride. It combines readily with S, P, As., and alloys freely with most metals. The alloys are much more fusible than the metal itself. Platinum salts are decomposed by heat, leaving the metal. A solution of platinic chloride gives the following reactions.

Wet Tests.—Sulphuretted hydrogen in hydrochloric acid solutions precipitates, on warming or standing, black platinic sulphide, which dissolves with some difficulty in yellow ammonium sulphide, and is thrown down again by hydrochloric acid. It is insoluble in nitric acid, but dissolves in aqua regia.

Ammonium chloride in *strong* solutions throws down a crystalline yellow precipitate of $2\text{NH}_4\text{Cl} \cdot \text{PtCl}_6$. The solution if dilute should be concentrated to small bulk, vigorously shaken after the addition of the chloride, and allowed to stand. The precipitate is insoluble in alcohol, which is therefore always added.

Stannous chloride produces a dark brown coloration, due to formation of platinous chloride.

Ferrous sulphate, oxalic acid, and other reducing agents do not precipitate platinum except on prolonged boiling. (Compare Gold.)

ESTIMATION OF PLATINUM.

The assay of platiniferous materials is rendered difficult, owing to the difficult fusibility of the metal and its resistance to chemical action, and to the great difficulty of accurate sampling.

1. **Assay of Platinum Sand.**—With platinum sand a preliminary “vanning” is necessary to concentrate the metal (see *Tin*). If already concentrated this is unnecessary. The concentrates are melted with lead, and the platinum determined in the alloy.

25–50 grms. of the ore is melted with six times its weight of assay lead in a carbon crucible at a high temperature and poured. The resulting button is cleared of any slag or adhering sand.

If arsenides or sulphides are present the alloy should be made on a scorifier and the slag removed very carefully, as the button will be brittle. In either case it must be accurately weighed.

Grind the button (if possible) in a mortar, and take portions for assay. These should represent not less than 0.05 gm., *i.e.* 50 mg.* of platinum. They are each scorified with 40 grms. of lead in the ordinary way (see *Silver*), but at the highest attainable temperature.

The button is cleaned of slag, and boiled with dilute nitric acid (1 part acid, 4 water) till action ceases. The solution is diluted to 250 c.c., and filtered through a small ashless filter paper. After washing by decantation, the residue is transferred to the filter, and dried. The filter and contents are placed in a wide porcelain crucible (previously weighed), and ignited, first over a burner, then in the muffle at a low heat for at least ten minutes to permit the oxidation of any lead left undissolved by the acid. The residue, after cooling, is warmed with dilute nitric acid, which is drained away from the platinum gold, remaining undissolved, washed by decantation, dried, and weighed.

It is then warmed with dilute aqua regia (1 in 6) for a few minutes to dissolve the gold and platinum, the liquor decanted and the treatment repeated. It is afterwards washed thoroughly by decantation, dried, and the residue weighed (see below).

The filtrate (gold and platinum) is evaporated just to dryness (finishing on a water-bath), the residue dissolved in water and one or two drops

* Russian ores usually contain about 80 per cent. of platinum.

dilute hydrochloric acid and diluted to 50 c.c. The gold is precipitated by warming with oxalic acid (crystals) for half an hour. The precipitated gold is filtered off through an ashless paper, dried, ignited, and weighed. Or it may be cupelled with silver and parted in the usual way. The platinum is determined by difference.

The platinum may be directly estimated by evaporating the solution to small bulk with strong nitric acid, adding finely powdered potassium chlorate, in small portions at a time, to destroy the oxalic acid. Ammonium chloride is then added, and alcohol, to the extent of twice the bulk of solution. The precipitated $(\text{NH}_4\text{Cl})_2\text{PtCl}_6$ is collected in a filter, washed with alcohol and ammonium chloride, and dried. The filter is placed in a porcelain crucible, ignited, and weighed, as Pt.

Notes.—In the scorification, iron, copper, and other base metals, as well as silica, are fluxed by the litharge, and some osmium is volatilized. On treating with nitric acid most of the lead, and all the silver, palladium, and some rhodium, are removed, leaving gold, platinum, iridium, iridosmium, and possibly ruthenium, rhodium, osmium, as well as some lead. After calcining, the second nitric acid treatment removes the lead, while the aqua regia dissolves gold and platinum, leaving the iridium and osmiridium, and most of the ruthenium and rhodium, if present. If it is required to separate the iridium from iridosmium after weighing the residue, treat with strong aqua regia. This dissolves the iridium, and osmiridium is left.

Assay of Platinum by Solution in Nitric Acid.—In this method advantage is taken of the complete solubility of platinum-silver alloys containing less than 9 per cent. of platinum in nitric acid.

The assay is conducted as follows:—After fusion with lead (see previous method), the scorification and cupellation are completed as usual, but at a higher temperature, with the previous addition of silver (or preferably gold), to the extent of five times the weight of platinum present. After brightening, the button is allowed to remain about ten minutes, to insure the complete removal of lead. The button is weighed, the silver or gold added, deducted, and the weight noted. The loss in weight is due to the base metals present.

The button is parted as for gold (inquarting previously, if gold were added instead of silver), or with sulphuric acid (concentrated) if silver were added.* The residue is collected, washed, and weighed (see Gold). The loss in weight, less the silver added, represents the silver in the ore plus palladium if present.

The remaining gold, platinum, iridium, osmiridium, from the parting is wrapped in lead foil with twelve times its weight of fine silver. This is dropped into a cupel containing 10 grms. of molten test lead, and cupelled at a high temperature.

The button is hammered, rolled out, and parted with nitric acid,

* To avoid possible solution of platinum.

sp. gr. 1.16, and afterwards with acid, sp. gr. 1.26. The boiling with acid is continued for some time. It is advisable to re-alloy with silver and re-part to insure the complete removal of the platinum, or the gold result will be too high. The residue is collected, washed, dried, and weighed. The loss is the platinum.

The gold is removed from the residue by treatment with dilute aqua regia (1 in 6), and the remaining osmiridium and iridium weighed, the loss being the gold. In assaying silver and gold ores containing platinum, the presence of small quantities will not be noticed, unless specially looked for. Larger quantities cause the button during cupellation to freeze, and at the end the surface will be broken up, and pitted or very much frosted. In such cases platinum must be searched for, and the assay modified by the addition of pure silver to prevent freezing. This must of course be deducted from the weight of silver obtained in the cupellation.

Cadmium prevents the solution of platinum in nitric acid. So that by the addition of this metal to a platiniferous alloy of gold and silver, on treating with nitric acid both gold and platinum remain (Rose, *Metallurgy of Gold*).

Wet Assay of Platinum.—5 or 10 grms. of the ore is boiled with hydrochloric acid, and the residue washed by decantation. It is then digested at a moderate temperature for twelve hours or so with aqua regia. The residue is filtered off and well washed. The solution, which contains platinum and gold, is evaporated nearly to dryness. A strong solution of ammonium chloride is then added, and absolute alcohol to about double the volume of the solution. It is then allowed to stand for some hours, filtered, the precipitate washed with ammonium chloride, dried, ignited, and weighed as platinum, as directed.

The filtrate from the ammonium platinum chloride may contain gold. This is precipitated with ferrous sulphate or oxalic acid, and the gold estimated, as directed (see Gold).

SULPHUR.

THE notice of sulphur under this heading will be confined to the estimation of sulphur in pyrites and other minerals. Other determinations of sulphur in fuels, metals, etc., will be found in Part III.

Estimation by Conversion into Sulphuric Acid and Sulphates.—

When sulphur or sulphides are heated with powerful oxidizing agents in the presence of strong bases, such as soda, potash, magnesia, and lime, the sulphur is completely converted into a sulphite or sulphate of the metal. In presence of sufficient oxidizing agent, sulphate only is produced; but if only an alkali or an insufficient amount of oxidizing agent be present, then the sulphite is produced in greater or less quantity. The addition of bromine to the solution obtained converts the sulphite into sulphate, the form in which sulphur is generally estimated in direct methods for its determination. In using oxidizing agents like potassium nitrate, chlorate, and caustic alkalies, there is always a tendency for the melted mass to creep over the side of the crucible. And there is danger of sulphur being taken up from the products of combustion of the burner, if coal gas is being used. With a spirit lamp, no such increase in sulphur takes place.

Estimation of Sulphur by Fusion with Potassium Chlorate and Carbonate, and Common Salt.—1 grm. of finely powdered pyrites is mixed with 8 to 10 grms. of a mixture of equal parts of potassium chlorate, sodium carbonate, and common salt. This is put into a deep crucible,* and carefully heated till quietly fused. The crucible is allowed to cool, the melted mass boiled out with water, the solution, together with any undissolved matter, being transferred to a half-litre flask, and made up to half a litre. After settling, the sulphuric acid is determined in 250 c.c. of the clear solution, decanted through a dry filter. The solution is slightly acidified with hydrochloric acid, heated to boiling, and the sulphuric acid precipitated by a strong boiling solution of barium chloride. After precipitation the liquor is boiled for about 10 minutes,

* An iron crucible may be employed.

filtered and washed. If due precautions have been taken, the precipitate will settle in a dense granular form, which filters and washes well. The essentials of success are hot solutions, a large excess of barium chloride, and only a small excess of hydrochloric acid. Nitric acid must be absent. The washing and filtration of the precipitate is in this case easy, as only salts of the alkalies are present. Hot water and a wash-bottle, with a very fine jet, are desirable. The precipitate is dried, ignited, and weighed as BaSO_4 , containing 13.75 per cent. of sulphur.

In some works the sulphide is mixed with ten to twelve times its weight of a mixture of potassium chlorate and sodium carbonate only, six parts of the latter to one of the former, the fusion being effected over a good foot blow-pipe, or in a muffle.

Estimation of Sulphur by Heating with Caustic Alkalies.—The substance is heated with caustic soda, potash, or with soda lime. The pyrites is reduced to the finest possible state of division, 0.25 grm. of pyrites, or a correspondingly greater quantity of a poorer material is fused with 25 grms. of pure potash or soda in a silver dish, the pyrites being added to the fused caustic. The whole is fused for twenty minutes, and after cooling, the mass is dissolved in cold water. The insoluble residue is filtered off, and well washed, 100 c.c. of bromine water added, and the solution made slightly acid with hydrochloric acid. The excess of bromine is removed by boiling, and the clear boiling solution precipitated by barium chloride as before.

If soda lime is used the pyrites must be ground with the lime, the mass after fusion treated with bromine water, and afterwards extracted with hydrochloric acid. It is not necessary to completely dissolve the residue, but a good deal of iron enters into the solution. This makes it a little difficult to get the precipitate quite white, but the iron can be dissolved out by treating the ignited precipitate with hydrochloric acid. The bromine and other reagents employed should be tested for sulphur.

VOLUMETRIC METHODS.

Estimation by Fusion with Sodium Carbonate and Potassium Chlorate.—1 grm. of the very finely powdered mineral is mixed with 2 grms. of potassium chlorate, 5 to 10 grms. of pure sodium carbonate (accurately weighed), and about 15 grms. of salt. The mixture is fused till all action ceases. The sulphur is oxidized, and, attacking the sodium carbonate, expels carbonic acid gas. The residue is dissolved

in water, and the excess of sodium carbonate used estimated by standard hydrochloric acid, using litmus or methyl orange as an indicator. If litmus be employed, the solution must be titrated boiling.

The acid used may be normal, *i.e.* containing 36.5 grms. of HCl per litre, and must be standardized by titrating weighed samples of pure sodium carbonate.

The sulphate formed may also be estimated by barium chloride (see above).

Wet Estimation (Wright's Process).—The pyrites is reduced to the finest possible state of division. One grm. is treated with strong nitric acid, and cautiously heated for a few minutes. Hydrochloric acid is then added, and gentle heating continued till the ore is dissolved. This is best done in a conical flask or a deep beaker. The solution is then evaporated to dryness, and heated till all nitrates are decomposed. The residue is moistened with hydrochloric acid and warmed till solution is complete, distilled water is then added till the solution occupies about 120 c.c., and then ammonia till nearly neutral. It is then heated to boiling, and titrated with standard barium chloride solution, containing 32.5 grms. of pure anhydrous barium chloride per litre, or 38.11 grms. of the crystallized salt; each c.c. of this solution is equal to 0.005 grm. sulphur. The titration is continued till no further precipitate is produced. The end is determined by filtering a small quantity of the solution into a clean test-tube, and testing it with a drop of the standard solution. If a precipitate is produced it is returned to the main bulk, shaken, and more barium solution added. This is repeated till the titration is complete. If too much barium chloride be added, it may be titrated back with a standard solution of sodium sulphate, the sulphur equivalent of which is exactly equal to the barium chloride solution. This is prepared by dissolving 50.31 grms. of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per litre. The end of the titration is determined in the same manner as before. Or 5 c.c. of the sodium sulphate solution may be added, and the solution again titrated with barium chloride. In calculating the sulphur the total bulk of the latter solution must be reduced by the amount of sodium sulphate solution added.

If the sulphur is to be determined gravimetrically, the liquid, after taking up with hydrochloric acid and diluting, is filtered free from silica, nearly neutralized, and a quantity of tartaric acid equal in amount to the iron present is added to keep the iron in solution before adding the barium chloride. If the precipitate is brown, it is washed at the end with hydrochloric acid and barium chloride till white, and finally with water.

A modification of Wright's process, which gives more satisfactory

and concordant results, is conducted as follows. The substance is fused with an oxidizing mixture, and the fused mass extracted with 300 or 400 c.c. water. About 10 grms. of solid sodium acetate and 10 c.c. of acetic acid are added, and the solution boiled and titrated.

If solution in nitrohydrochloric acid be adopted, the nitric acid must be removed by evaporation with hydrochloric acid, 20 grms. of sodium acetate added to the solution, which is diluted to 500 c.c., heated to boiling and titrated. If not still strongly acid, after adding the sodium acetate about 5 c.c. of acetic acid should be added before titrating.

Estimation of Sulphur in Burnt Pyrites.—5 grms. of the pyrites cinders are fused with 15 grms. of the potassium chlorate fusion mixture (see *ante*) in a deep crucible. The fused mass is extracted with water, sodium acetate and acetic acid added as before, and titrated. The sulphur in burnt ore seldom exceeds 4 per cent.

The above methods yield fairly good results in the absence of lead.

If lead be present, the ore may be oxidized by reducing it to the finest possible state of division, sifting it through muslin (see chrome iron ore), and suspending it in caustic potash solution, through which a stream of chlorine gas is slowly passed. The lead separates in the insoluble residue as dioxide. The alkaline liquor is nearly neutralized with hydrochloric acid, decanted through a filter, and the residue washed. A slight excess of hydrochloric acid is then added, and the solution titrated as before, or precipitated with barium chloride and the sulphate weighed.

This method is not suitable for determination of ores containing much silica. Siliceous ores containing lead are best dissolved in hypochlorous acid.

Solution in Bromine Water.—The pyrites is very finely powdered, suspended in water, 100–120 c.c., and for each gramme of pyrites, 8–10 grms. of bromine is added. The action proceeds freely, but near the end gentle warming on the water-bath is necessary. Excess of bromine is boiled off, the silica removed (if the sulphur is to be determined gravimetrically), the liquid nearly neutralized with ammonia and precipitated or titrated as before. The decomposition should be effected in about half an hour.

Estimation of Sulphur in Sulphates.—For soluble sulphates dissolve in a suitable solvent and proceed as for solutions. For barytes (BaSO_4) 2 grms. of the mineral is fused with 8 grms. of a mixture of equal parts potassium and sodium carbonates for ten minutes. The fused mass is extracted with water, filtered and washed, and the sulphur determined in the aqueous solution. Lead sulphate may be treated in the same way, or may be dissolved in ammonium acetate.

Molybdate Method.—An ingenious method of determining sulphur is suggested by Furman. It is an adaptation of Alexander's method for estimating lead by ammonium molybdate (see p. 66). The sulphur is converted into sulphuric acid, a known weight of lead nitrate added, and the sulphate formed determined.

The molybdate solution is standardized by pure lead sulphate (see p. 66), and the lead equivalent calculated into sulphur. Thus, if 1 c.c. of the solution = 0.01 of Pb or 0.01464 grms. of PbSO_4 , the factor for sulphur in PbSO_4 = $0.1056 \therefore 0.01464 \times 0.1056 = 0.001546$ S.

The sulphur in the pyrites, matte, or other material is oxidized by any of the ordinary methods, *e.g.* fusion with caustic potash, with the caustic potash, soda, magnesia mixture (see p. 365), by roasting with magnesia, by fusion with Na_2CO_3 , NaCl , and KNO_3 , or in the wet way by aqua regia, chlorate of potash, etc., as described.

The melt or solution is treated in the ordinary way up to the point of precipitation. In all roasting operations where nitre does not enter into the mixture after boiling with water, peroxide of hydrogen must be added in place of bromine to ensure complete oxidation, and in wet treatment all excess of acid must be removed. Chlorides are preferably absent, and nitric acid should be used for acidification.

After boiling out the melted mass or evaporating to dryness with excess of nitric acid after solution in aqua regia, the solution is very slightly acidified with nitric acid. Excess of a solution of pure lead nitrate is then added to the hot solution, and the precipitate of lead sulphate allowed to settle. It is thoroughly washed by decantation till the washings are free from lead. Any precipitate on the paper is washed back into the beaker by a jet of weak ammonia, some strong ammonia added, and then acetic acid till slightly acid. The beaker is warmed till the precipitate of lead sulphate is dissolved, and the titration with ammonium molybdate conducted in the usual way (see p. 66).

Reports.—In reporting sulphur, regard must be had to the character of the material and the uses for which it is intended. Thus in reporting on mattes and sulphide ores, "total" sulphur would be required. When the material contains both sulphides and sulphates, *e.g.* galena associated with barytes, it is necessary to report sulphur as sulphide and sulphur as sulphate, reported as SO_3 , sufficient of the base being reported as oxide as is required to combine with the SO_3 .

In the above instance two methods are followed. Method I.—Two grms. of the mineral (galena) in a fine state of division is placed in a beaker covered with fuming nitric acid, and warmed. Small fresh additions of nitric acid and a few small pinches of finely powdered potassium chlorate are made from time to time till all black residue

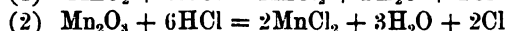
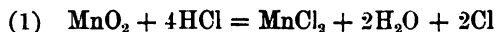
has disappeared. The residue is evaporated with nitric acid to remove chlorine, lead nitrate added, diluted to 50 c.c., boiled, allowed to settle, and the residue filtered, and washed by decantation. The lead sulphate is removed and the lead estimated as detailed in the molybdate method given above. From the amount of lead the sulphur is calculated. It represents the sulphur existing as sulphides and lead sulphate. A determination of total sulphur is also made by fusion, and the difference between that found in the lead sulphate and the total is returned as SO_2 in barium sulphate. The mineral should be tested for lead sulphate, by extraction with ammonium acetate, before treatment with nitric acid, and the lead determined in the filtrate and calculated to sulphate.

Method II.—Only applicable in the absence of metallic sulphides other than lead. The sulphur existing in the galena as sulphide is got rid of as sulphuretted hydrogen by treatment with hydrochloric acid and zinc. The residue is filtered and washed. The filtrate is tested for sulphate with barium chloride. The precipitated lead and insoluble residue are treated with dilute nitric acid, and the residue filtered and washed. It is dried and fused with sodium and potassium carbonates, and the sulphur it contains estimated by precipitation with barium chloride as sulphur in sulphates. An estimation of total sulphur is made, and the difference gives the sulphur as sulphide. If lead sulphate is suspected, it must be separated from a separate portion by ammonium acetate, estimated by molybdate, and deducted, reporting S as sulphide, SO_2 in lead sulphate, and SO_2 in barium sulphate.

ESTIMATION OF CHLORINE.

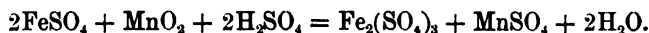
IN the chlorination of gold ores, chlorine is prepared by the action of hydrochloric acid (or sulphuric acid and salt), on oxide of manganese, or by the action of sulphuric acid on bleaching powder. As the amount of chlorine which will be evolved depends on the composition of the materials used, a determination of the available chlorine is always advisable.

ASSAY OF MANGANESE DIOXIDE.—Several oxides of manganese occur in nature, and, as these produce different quantities of chlorine when treated with hydrochloric acid, *e.g.*—



a determination of the manganese does not give the information required, and the chlorine evolved must be determined.

(1) **Iron Method.**—This is the usual method employed for the valuation of manganese ores. It depends on the fact that if peroxide of manganese be mixed with sulphuric acid and ferrous sulphate, the iron is oxidized to the ferric condition—



If excess of the iron salt be employed, the excess can be determined volumetrically, and the amount of manganese peroxide in the ore calculated. The materials required are pure iron sulphate, ammonium ferrous sulphate, or a solution of a ferrous salt, the strength of which is accurately known, and a standard solution of potassium bichromate or potassium permanganate as used for the determination of iron (p. 177).

One gram. of the ore, finely powdered in an agate mortar, is introduced into a flask fitted with a Bunsen valve (Fig. 73, p. 173), and 10 grms. of ferrous ammonium sulphate or a quantity of a solution of a ferrous salt, containing about 1.5 gram. of iron in the ferrous condition, is added, then about 20 c.c. of strong sulphuric acid, and warmed till solution is complete. The ferrous iron is then estimated in the usual way, and the amount of iron found is deducted from that added. The remainder

has been oxidized during the solution. Each 0.1 gm. of iron oxidized is equivalent to 0.12873 gm. of dioxide of manganese, and 0.0816 gm. of chlorine. From this the chlorine generating value is calculated (p. 202).

(2) **Estimation by Oxalic Acid.**—This method depends on the oxidation of oxalic acid by means of the oxygen liberated from the oxide of manganese by treatment with sulphuric acid.

One gm. of the ore, very finely powdered, is weighed into a flask, covered with water, 25 c.c. of a solution of oxalic acid of known strength (90 grms. per litre) is added, and 5 c.c. of strong sulphuric acid, and warmed gently till solution is complete. If the solution contains any dark coloured matter, this is filtered off, and the solution titrated with a standard solution of potassium permanganate.

The potassium permanganate solution being at the same time titrated against the solution of oxalic acid employed, the amount of oxalic acid oxidized can be at once ascertained, and each 0.1 of oxalic acid used is equivalent to 0.0967 gm. of dioxide of manganese or 0.0789 of chlorine.

BLEACHING POWDER.—Commercial bleaching powder is frequently used as the source of chlorine. It is of uncertain composition.

Whatever method is followed for determining the available chlorine, the first thing is to get the sample into solution, and as the material is hygroscopic and unstable, this should be done as quickly as possible. 7.17 grms. of the powder is quickly weighed, put into a porcelain mortar, a little water added, and rubbed into a cream. This is allowed to settle for a few minutes, the solution poured into a litre flask, the residue again treated in the same manner, the solution poured off, and this operation repeated till all the powder is transferred to the flask. The mortar is rinsed, and the flask filled up to the mark.

(1) **Arsenious Acid Method**—This depends on the oxidation of arsenious acid to the arsenic condition by the bleaching powder, the slightest excess of the latter being detected by its action on iodide of potassium in presence of starch.

The requirements are (1) Standard decinormal ($\frac{N}{10}$) solution of arsenious acid. This is made by dissolving 4.95 grms. of the purest sublimed white arsenic, finely powdered, in 250 c.c. of water, with the addition of about 20 grms. of pure potassium bicarbonate, warming if necessary, and diluting to a litre in the cold. (2) Iodized starch paper. This is prepared by adding a little potassium iodide solution to thin starch solution (p. 228) and soaking strips of filter paper in it. These are best laid on a glass plate and used moist.

The flask containing the bleaching powder solution is well shaken, and 50 c.c. of the turbid solution measured into a basin. The standard solution is then added, till a drop of the solution put on the starch paper just ceases to give a blue coloration. Each c.c. of the arsenite solution used = 1 per cent. of available chlorine.

The process may be modified by adding excess of the arsenious acid solution, then adding a little starch paste and titrating back with $\frac{N}{10}$ * iodine solution till a blue colour is produced.

(2) **Bunsen's Method.**—This depends on the liberation of iodine by the bleaching powder. The requisites are a solution of potassium iodide and a solution of sodium thiosulphate, about $\frac{N}{10}$, *i.e.* 24.8 grms. per litre, but as the solution is unstable, it must be standardized frequently against pure copper or pure iodine (see p. 86).

Make the solution of bleaching powder exactly as above, except that 10 grms. may be used. Take 50 c.c. of the solution = 0.5 gm. of the powder, and add about 3 grms. of potassium iodide, shake and titrate with the sodium thiosulphate, using starch solution as indicator.

Each 0.1 gm. of iodine is equivalent to 0.028 gm. of available chlorine, from which the percentage may be calculated (see also p. 203).

* 12.653 grms. per litre.

PART III.

EXAMPLES OF METALLURGICAL
ANALYSIS

METALS AND ALLOYS OTHER THAN IRON AND STEEL

BRASS.

1. BRASS is essentially an alloy of copper and zinc, but it always contains small quantities of other substances, either as impurities or added intentionally. The copper varies from about 50 per cent. to 90 per cent. The lead present should only be that derived from the spelter used, and should never exceed 1 per cent. even in a brass containing a low percentage of copper.* Iron should not exceed 0.25 per cent., and is entirely derived from the tools used for stirring the metal, or otherwise accidentally introduced. Tin should be absent, and the alloy should dissolve completely in nitric acid. Should tin be present, the method for bronze (p. 294), must be used. For ordinary purposes a determination of copper, zinc, lead, and iron is all that is required. Other metals, such as arsenic, bismuth, etc., may be present in small quantity, and, when required, may be estimated as directed on p. 311 for commercial copper.

Method 1.—Copper.—Weigh out three portions of the alloy, each weighing about 0.5 grs., and put them into 16-ounce flasks. Dissolve in a few drops of strong nitric acid; warm till solution is complete, and the brown nitrous fumes are all expelled. Neutralize with a saturated solution of sodium carbonate, adding it drop by drop till a permanent precipitate is produced, and dissolve this by adding dilute acetic acid (1:4) drop by drop till the precipitate is just redissolved. Then add 3 grms. of potassium iodide, and titrate with sodium hyposulphite, as directed on p. 86.

The results should not differ by more than 0.15 per cent.

Lead and Zinc.—Dissolve about 1 grm. of the alloy in 10 c.c. strong nitric acid in a small beaker. When solution is complete, add about

* Very poor brasses often contain as much as 4 per cent. lead.

5 c.c. of strong sulphuric acid, and evaporate on the hot plate till fumes of sulphuric acid are given off; let cool, and, when cold, add a little warm water, and warm till the copper salts are all dissolved, and the residue is quite white. Filter through a small filter into a No. 6 beaker, wash with very dilute (2 per cent.) sulphuric acid till the precipitate is free from copper, then with dilute alcohol—collecting the alcoholic washings in a separate beaker as they may be rejected—till the filtrate is no longer acid. Dry the precipitate in the water bath, transfer it to a porcelain crucible, and burn the filter paper on the crucible lid. When all the carbon is consumed, moisten the residue with nitric acid, and warm; then add a drop or two of sulphuric acid and carefully evaporate to dryness. Put the lid on the crucible inverted, heat gently, and weigh the PbSO_4 . Factor for Pb = 0.68295.

Separation of the Copper.—To the filtrate from the lead sulphate add about 50 c.c. of a solution of potassium metabisulphite and potassium sulphocyanate (100 grms. of each per litre), and warm gently. Filter, and wash with water containing a little of the metabisulphite-sulphocyanate solution.

If it be desired to estimate the copper in the same portion, ammonium salts should be used for the precipitation. The precipitate is dried, transferred to a porcelain crucible, the paper burned, and the ash added. One grm. of sulphur, which must leave no residue on ignition, is added, and the whole ignited in a stream of hydrogen till the weight is constant. The residue is cuprous sulphide, Cu_2S . Factor Cu = 0.79834.

Estimation of the Zinc.—Heat the filtrate from the cuprous sulphocyanate precipitate to boiling, add sodium carbonate in excess; boil, filter, wash thoroughly till the washings are free from solid matter in solution, and dry the precipitate in the steam bath.

Transfer the dried precipitate as completely as possible to a porcelain crucible; burn the paper, and collect the ash on the crucible lid, moisten the residue with nitric acid, and heat gently till all the acid is expelled; then put the lid on the crucible and ignite strongly, finishing the ignition over the foot blow-pipe, till the weight is constant.

The ignited precipitate is zinc oxide, ZnO , but it also contains any iron originally present in the alloy. In ordinary cases this may be neglected; but where it is necessary to take it into account, dissolve the ignited precipitate in hydrochloric acid, heat to boiling, add ammonium chloride, then ammonia in excess, boil, and filter. Dissolve the precipitate in hydrochloric acid, reprecipitate, wash, dry, ignite, and weigh the ferric oxide. Deduct the weight obtained from that of the zinc oxide, and calculate the zinc from the weight thus obtained. Factor for Zn = 0.80263.

Zinc may also be estimated by means of standard ferrocyanide solution (p. 239).

Iron.—Dissolve 5 or 10 grms. of the alloy in nitric acid ; when solution is complete dilute to about 200 c.c., add 10 grms. of ammonium chloride, then ammonia in excess ; heat to boiling, filter, and wash. Dissolve the precipitate of ferric hydrate, which still retains some copper and lead, in dilute hydrochloric acid, dilute, saturate with sulphuretted hydrogen, and let stand for half an hour. Filter, and wash. The precipitate may be rejected. Boil the filtrate till all sulphuretted hydrogen is expelled, add a little strong nitric acid to convert the iron into a ferric salt, add ammonia in excess, boil, filter, wash, dry, ignite, and weigh as ferric oxide. Factor for Fe = 0.7.

Method 2.—Preparation.—Weigh 1 grm. of the alloy and dissolve it in a small quantity of nitric acid.

Lead.—Separate and estimate the lead exactly as described in the first method.

Copper.—Dilute the filtrate from the lead sulphate precipitate, to about 200 c.c., nearly neutralize with caustic soda, heat to boiling, and add a strong solution of sodium thiosulphate (sodium hyposulphite) till, on standing, the black precipitate settles, leaving the solution milky. Filter, wash thoroughly with hot water, and dry the precipitate. Transfer the dried precipitate to a porcelain crucible, burn the paper, and add the ash, cover with a layer of pure sulphur and a lid, and ignite in a stream of hydrogen, or in a muffle, till no more sulphur is evolved. Cool, and weigh the cuprous sulphide (Cu_2S).

Separation of the Zinc and Iron.—Heat the filtrate from the cuprous sulphide nearly to boiling, and add hydrochloric acid drop by drop till the hyposulphite is all decomposed. Add a little nitric acid to peroxidize iron, and boil, then add ammonia in excess, boil, filter, wash, and weigh the ferric oxide.

Estimation of the Zinc.—Heat the filtrate from the ferric hydrate precipitate to boiling, and add ammonium sulphide solution in small quantities till precipitation is complete, boil for a few minutes, filter hot, and wash with water containing ammonium sulphide. Dissolve the precipitate in dilute hydrochloric acid, boil the solution till all sulphuretted hydrogen is expelled. Then add sodium carbonate in excess ; boil, filter, wash, dry, ignite, and weigh as zinc oxide, as described under the first method. Or the zinc may be estimated by standard ferrocyanide, as described on p. 239.

BRONZES.

2. Bronze is essentially an alloy of copper and tin, with or without zinc, and with only small quantities of other metals. In many bronzes, such as gun-metal, etc., zinc is absent; in others, as in our coinage alloys, it is present in small quantities (about 1 per cent.), whilst in others, which are called commonly, almost indiscriminately, brass or bronze, it may be present up to about 25 per cent. For analytical purposes all copper alloys containing tin may be called bronzes.

The metals which have to be determined are usually tin, copper, lead, iron, and zinc.

Method 1.—Copper.—Weigh out three portions of about 0.5 gm. each into very small beakers, dissolve in a few drops of strong nitric acid, and heat gently on the hot plate till solution is complete and the nitrous fumes are expelled. Then add about 20 c.c. of hot water, filter through very small papers into 16-ounce flasks, wash with the smallest possible quantity of hot water. Let the filtrate cool, and proceed exactly as described for brass (p. 291).

As the presence of metastannic acid does not interfere with the determination of the copper by thiosulphate, the filtration is not essential, and solution may be effected directly in the flasks, but the presence of the white metastannic acid makes it more difficult to determine when the solution of the copper carbonate precipitate in acetic acid is complete.

Tin, Lead, Zinc, and Iron.—Weigh 1 gm. of the alloy and dissolve it in strong nitric acid; heat till solution is complete, and evaporate till copper salts begin to crystallize out. Then add 50 c.c. of water, and a few drops of nitric acid, if necessary; boil, filter, wash thoroughly, dry, ignite, as directed for zinc (p. 292), and weigh the tin oxide, SnO_2 . The ignited oxide should be white or pale yellow; if it be dark coloured, the copper has not been completely removed.

Lead, Zinc, and Iron.—Proceed exactly as directed for brass (p. 292), using the filtrate from the metastannic acid.

Method 2.—Weigh 1 gm. of the alloy and dissolve it in aqua regia (1 part HNO_3 , 4 parts HCl) in a No. 4 or No. 5 beaker, using as little acid as possible, and heat till all the nitric acid is expelled.

Separation of the Tin.—Dilute the solution to about 200 c.c., add ammonia till a permanent precipitate forms, then hydrochloric acid drop by drop, till it is dissolved. Then add a strong solution of ammonium nitrate, heat to boiling, and let stand on a hot plate for an hour. When the precipitate has settled, add to the clear solution a little more ammonium nitrate, and should no further precipitate fall, filter, and wash well with hot water.

Estimation of the Tin.—Dry the stannic hydrate precipitate, ignite, as previously directed, and weigh the stannic oxide, SnO_2 .

Estimation of the Lead, Copper, etc.—To the filtrate from the tin precipitate add a little sulphuric acid and evaporate till fumes of sulphuric acid are evolved. Estimate the lead, copper, zinc, and iron exactly as directed for brass (p. 293).

3. DELTA METAL.—This is an alloy of copper, tin, and zinc, containing a considerable quantity of iron.

It may be analyzed exactly as described for bronze, Method 1, but the stannic oxide, after weighing, must be examined for iron, the weight of the ferric oxide must be deducted from that of the stannic oxide, and the iron added to that obtained in the filtrate.

Examination of the Stannic Oxide Precipitate for Iron.—Powder the precipitate, mix it with 2 grms. of sodium carbonate and 2 grms. of sulphur, and fuse in a porcelain crucible. Let cool, boil with water till solution is complete, then filter, and wash well. The tin sulphide formed in the fusion is dissolved in the sodium sulphide also produced, leaving the iron sulphide as an insoluble residue. Dissolve the black residue in hydrochloric acid, boil, add a little strong nitric acid to convert the iron into a ferric salt, then add ammonia in excess, boil, filter, wash, dry, ignite, and weigh the ferric oxide.

4. ALUMINIUM BRASS, OR BRONZE.—Aluminium bronze is essentially an alloy of copper and aluminium, whilst aluminium brass contains zinc in addition. Tin may be present, and there are usually traces of iron and lead.

Tin and Copper.—These are estimated exactly as in ordinary bronzes.

Aluminium and Zinc.—Weigh out 1 gm. of the alloy, dissolve it in nitric acid, add a little sulphuric acid, and evaporate till nitric acid is completely expelled, then dilute, warm to about 70°C ., and saturate with sulphuretted hydrogen. Let stand for half an hour, filter and wash thoroughly with water containing sulphuretted hydrogen. The precipitate may be rejected, the filtrate will contain aluminium and zinc. Boil till all sulphuretted hydrogen is expelled, add ammonia till a permanent precipitate forms, then dilute hydrochloric acid till it is just redissolved, and heat to boiling. Add about 5 grms. of ammonium or

sodium acetate, and boil for two or three minutes. Let the precipitate settle, filter, wash once or twice by decantation, then on the filter. To the filtrate add 2 grms. more of the acetate, and again boil. Should a further precipitate come down, filter again, and repeat till addition of acetate and boiling produces no further precipitate.

Estimation of the Aluminium.—Dissolve the precipitate of basic aluminium acetate in hot dilute hydrochloric acid, add ammonia in excess, and boil till the solution ceases to smell of ammonia, wash, dry, ignite, and weigh the alumina (Al_2O_3).

The precipitate will contain any iron that may have been present in the alloy, as oxide. The amount of this will always be small; but if an accurate analysis be required it must be estimated, and its weight deducted from that of the alumina before calculating the latter to aluminium. Factor for Al = 0.58279.

Estimation of the Iron.—Powder the ignited precipitate of alumina, mix it with about 2 grms. of pure caustic soda in a silver basin, and fuse for about fifteen minutes, dissolve with hot water, filter, and wash. The aluminate of soda formed is soluble. Dissolve the residue of ferric oxide in strong hydrochloric acid, dilute, add ammonia in excess, boil, filter, dry, ignite, and weigh the ferric oxide.

Should the ferric oxide not be of its proper dark-brown colour, the fusion with soda must be repeated. This will not be necessary if the ignited oxide is well powdered before fusion, and the fusion continued sufficiently long.

Estimation of the Zinc.—Heat the filtrate from the alumina precipitate to boiling, add ammonia in slight excess, and while still boiling saturate with sulphuretted hydrogen, allow the precipitate to settle, and wash, first by decantation, then on the filter. Wash the precipitate back into the beaker, and dissolve it in hot dilute hydrochloric acid, and also dissolve any portions that remain adherent to the filter paper. Warm the solution till sulphuretted hydrogen is expelled, then add sodium carbonate in excess, boil, filter, wash, dry, ignite, and weigh the zinc oxide. Or determine the zinc in the solution by titration with potassium ferrocyanide solution (p. 289).

5. PHOSPHOR BRONZE.—This is bronze containing a small quantity of phosphorus, usually not more than 0.1 per cent.

The general analysis is conducted exactly as for ordinary bronze, but the tin oxide produced by the treatment with nitric acid contains all the phosphorus as tin phosphate. The phosphorus must, therefore, be determined, and the weight of the phosphoric anhydride (P_2O_5) deducted from that of the precipitate before calculating the tin.

Determination of the Phosphorus.—Weigh 10 grms. of the alloy,

heat with strong nitric acid, evaporate off the excess of acid, dilute, filter, and wash.

Wash the precipitate into a large porcelain basin, cover with water, add pure solid caustic soda, and warm until the tin oxide is almost all dissolved, then add yellow sodium sulphide, and digest for two hours at a gentle heat. Filter and wash. If a large residue remains, wash it back into the basin, and repeat the digestion with sodium sulphide.

To the filtrate add acetic acid in excess, let stand in a warm place for an hour or so, filter, taking care to disturb the precipitate as little as possible, wash once or twice by decantation, then on the filter, using salt solution for the final washing.

Boil the filtrate till sulphuretted hydrogen is expelled, and evaporate to small bulk. Add ammonia in excess, then "magnesia mixture," stir well, let stand for twelve hours, filter, wash with ammonia water, dry, ignite, and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$ (see p. 358).

As the filtration of the sulphide is often very troublesome, the following method may be adopted. Dilute the solution containing the tin sulphide precipitate to 500 c.c. Let settle, and decant through a dry filter till 250 c.c. have passed through. Estimate the phosphorus in this. The bulk of the tin sulphide may be neglected, and the solution will correspond to 5 grms. of the alloy.

6. OTHER SPECIAL BRONZES.—Among these may be mentioned silicon and manganese bronze; the important constituent of each is indicated by the name. The quantity of silicon and manganese is always very small, and often none can be detected.

The general analysis may be made as directed for bronze or brass, according as tin is present or not, a special examination being made for the element suspected.

Silicon.—Dissolve 10 grms. of the alloy in aqua regia, and evaporate to absolute dryness, let cool, take up with hydrochloric acid, and again evaporate to dryness, then add a little hydrochloric acid and water, and heat till solution is complete. Filter, dry, ignite, and weigh the silica. Transfer the silica to a weighed platinum dish, cover with hydrofluoric acid, or sulphuric acid and ammonium fluoride, and evaporate to dryness. Ignite, and weigh again. The loss of weight is the silica from which the silicon is calculated. Factor for Si = 0.46729.

Manganese.—Weigh 10 grms. of the alloy, treat with nitric acid, and separate the tin, lead, and copper as directed for bronze. Boil the filtrate from the copper sulphide precipitate, till all sulphuretted hydrogen is expelled. Add ammonia till a precipitate forms, then hydrochloric acid till the precipitate just redissolves, then about 5 grms. of sodium acetate, and boil. Filter off the precipitated basic ferric acetate,

and wash. To the filtrate add a little bromine, shake till it is dissolved, then add ammonia in excess, heat to boiling, and stand aside. Manganese, if present, will be precipitated as MnO_2 . Filter, dry, ignite, and weigh as Mn_2O_3 . Factor for Mn = 0.72029.

7. GERMAN SILVER.—This is one of a large number of alloys, known by various names, which consist essentially of copper, nickel, and zinc. They are largely used for the manufacture of table articles which are to be silver-plated.

Tin.—Estimate as directed for bronze.

Copper and Iron.—Estimate as directed for bronze.

Lead, Nickel, Zinc.—Dissolve 1 grm. of the alloy in 5 c.c. nitric acid, and dilute to 25 c.c. Remove tin hydrate, if present, by filtration, then the lead, by evaporation with sulphuric acid, as directed under Bronze, and the copper with sulphuretted hydrogen.

The filtrate from the copper sulphide precipitate contains the zinc, nickel, and iron. Boil till all sulphuretted hydrogen is expelled, and evaporate to about 100 c.c. Add carbonate of soda in excess, *i.e.* till all the metals are precipitated, then add acetic acid till the precipitate is redissolved. Pass sulphuretted hydrogen in the cold till the zinc seems to be all precipitated, and the solution, after standing a few minutes, smells strongly of sulphuretted hydrogen; then add a few drops of a 10 per cent. solution of sodium acetate, and pass sulphuretted hydrogen for a few minutes more. Let stand in a warm place for twelve hours, filter, and wash with water containing sulphuretted hydrogen.

Estimation of the Zinc.—Either dissolve the precipitate of zinc sulphide in hydrochloric acid, and reprecipitate with sodium carbonate, as directed on p. 293, or dry the precipitate, and transfer it to a porcelain crucible, burn the filter paper, and add the ash, cover the precipitate with sulphur, put the lid on the crucible, heat till the excess of sulphur is expelled, and weigh as zinc sulphide. Or the solution in hydrochloric acid, after boiling off H_2S , may be titrated with a standard solution of potassium ferrocyanide (p. 239).

Estimation of the Nickel.—Boil the filtrate from the zinc sulphide precipitate till all hydrogen sulphide is expelled, and evaporate to small bulk, put excess of caustic soda solution into a large nickel basin, and pour in the solution, rinsing the beaker well, heat to boiling, dilute the solution, if necessary, filter, wash thoroughly, dry, ignite, and weigh the nickel oxide. (See also p. 193.)

If cobalt be suspected, it may be estimated in the nickel precipitate as directed on p. 195.

WHITE METALS.

8. SOLDERS.—The alloys used for soldering purposes, as a rule, contain only tin and lead, with small quantities of other metals present as impurities.

Preparation and Solution.—Weigh 1 grm. of the alloy, in turnings or shavings, transfer to a beaker, cover with nitric acid, 1·2 specific gravity, and heat on the hot plate or sand-bath till all action ceases, evaporate till most of the acid is expelled, then dilute, boil, filter, and wash.

Estimation of the Tin.—Dry the precipitate, transfer it to a porcelain crucible, ignite as directed on p. 295, and weigh as stannic oxide, SnO_2 .

Estimation of the Lead.—Evaporate the filtrate till lead nitrate begins to crystallize out, then add 50 c.c. of water to dissolve the salt, a little strong sulphuric acid, and alcohol till the solution is about double its initial volume, heat to boiling, and let stand for an hour or so, filter, wash first with water containing a little sulphuric acid, then with alcohol and water till the washings are no longer acid, dry, ignite, and weigh the lead sulphate as directed on p. 291.

9. WHITE METALS.—A large number of these alloys are used for bearing metals and other purposes. They almost always contain copper, tin, lead, and antimony, sometimes iron and zinc, and more rarely other metals. It is stated that some of these alloys contain graphite; this is certainly not correct, but bismuth is frequently present. In addition to bearing metals, pewter, Britannia metal, type metal, etc., may be analyzed by the same method. The principal difficulty in the analysis is the separation of the antimony and tin.

METHOD 1.—Weigh 1 grm. of the alloy into a small beaker, cover with about 20 c.c. of nitric acid, 1·2 sp. gr., and heat on the hot plate till action ceases, then dilute to about 100 c.c. with hot water, boil, let settle, filter, and wash with hot water, twice by decantation, then on the filter. The precipitate contains the tin and antimony, the filtrate contains the copper, lead, zinc, etc.

Separation of Antimony and Tin.—Dry the precipitate, grind it in an agate mortar, transfer it to a silver basin containing 10 to 25 grms.

of pure sodium hydrate (potassium hydrate will not do), burn the filter paper, add the ash, and fuse for about 20 minutes. Let cool, and dissolve in a mixture of 2 parts water and 1 part alcohol, and stir till all soluble matter seems to be dissolved, then add more alcohol and water, and let stand for 12 hours. The tin is in solution as sodium stannate, the antimony is in the insoluble residue in the form of sodium meta-antimoniate. Filter, wash with dilute alcohol (1 in 3), and finally with strong alcohol.

Estimation of the Antimony.—Dissolve the precipitate in a little hot strong hydrochloric acid, to which a little solid tartaric acid has been added, in a small flask, dilute to about 100 c.c., warm, and pass a rapid current of sulphuretted hydrogen. When precipitation is complete, cork the flask so as to exclude air, then stand in a warm place for half an hour, filter as quickly as possible, wash with sulphuretted hydrogen water, and dry the precipitate in the steam bath. Remove the dry precipitate as completely as possible from the paper, and transfer it to a large weighed porcelain crucible. Should a sensible quantity of sulphide remain adherent to the paper, dissolve it in a drop or two of ammonium sulphide, let the solution run into the crucible, and dry it in the water bath. Burn the paper and add the ash. Moisten the precipitate with a drop or two of strong nitric acid, then cover with red fuming nitric acid (1.5 sp. gr.), evaporate very gently to dryness, and ignite cautiously at first, then at a full red heat, cool, and weigh as Sb_2O_3 . Use a deep crucible. Factor for Sb = 0.7922.

Or the sulphide may be dissolved in hot, strong hydrochloric acid, and the antimony estimated by potassium iodide and sodium thio-sulphate, as directed on p. 260.

Estimation of the Tin.—Boil the filtrate from the sodium antimoniate till all the alcohol is expelled, add slight excess of hydrochloric acid, dilute to about 100 c.c., and saturate with sulphuretted hydrogen. Let stand in a warm place for half an hour, filter, wash with sulphuretted hydrogen water, and dry at 100° . Transfer the dried precipitate to a porcelain crucible, burn the filter paper, and add the ash, heat, very cautiously at first, with the lid on the crucible, then more strongly with free access of air until no more sulphur dioxide is given off; then let cool, cover the residue with ammonium carbonate, cover the crucible, and heat till all the ammonium carbonate is expelled, cool, and weigh. Repeat the treatment with ammonium carbonate till the weight is constant.

The determination of tin in this manner is tedious. It may be estimated by difference if the precipitate of tin and antimony oxides, obtained by treatment with nitric acid, is dried, ignited, and weighed, and the antimony afterwards determined as directed.

Copper, Lead, etc., may be estimated in the filtrate from the tin and antimony oxides exactly as directed for bronze (p. 298).

Estimation of Bismuth.—Bismuth is often present in white alloys, and should always be looked for in bearing metals and solders.

Weigh 10 grms. of the alloy, dissolve it in aqua regia, and dilute the solution considerably. Add ammonia in slight excess, then yellow sulphide of ammonium, warm and filter, and reject the filtrate. Wash the precipitate back into the beaker, digest for an hour with ammonium sulphide, filter and wash with water containing ammonium sulphide. Wash the precipitate into a beaker, add strong nitric acid and boil, evaporate till most of the acid is expelled, then add sulphuric acid, and only enough water to enable the solution to be filtered, filter and wash with water containing sulphuric acid. To the filtrate add ammonium carbonate, then ammonia in excess, boil and filter; dissolve the precipitate in as small a quantity of nitric acid as possible, evaporate to very small bulk. The solution should be almost syrupy; then pour into a litre of water, and let stand. Decant off the clear solution, filter, and dry in the water-bath. Remove the precipitate as completely as possible from the filter paper, treat paper as directed for zinc (p. 292), ignite and weigh as Bi_2O_3 . Factor for Bi = 0.89767.

If the quantity of precipitate is very small, dissolve it into a weighed crucible by pouring a few drops of warm dilute nitric acid over the filter paper. Evaporate to dryness on the water-bath, ignite and weigh.

METHOD 2.—Weigh 1 grm. of the alloy, transfer to a small porcelain basin, add 4 grms. of solid tartaric acid, then 30 c.c. of nitric acid, sp. gr. 1.2, warm on the hot plate till all action ceases, and heat till excess of acid is expelled. Add a little water, and warm till any lead nitrate that may have crystallized out is dissolved, add a concentrated solution of potassium hydrate, and warm till the residue is dissolved, then add yellow sodium sulphide solution. Keep warm on the hot plate for three hours, but do not let the temperature rise to boiling. Let the precipitate settle, pour off the clear solution through the filter, wash once by decantation, then add a little more sodium sulphide, digest for two hours, dilute, filter, and wash, first by decantation, then on the filter, with water containing sodium sulphide. Mix the two filtrates.

Separation of Antimony and Tin.—Acidify the solution with hydrochloric acid, taking care not to add a large excess, and stand in a warm place till the odour of sulphuretted hydrogen has nearly disappeared. Filter, wash once or twice by decantation, then on the filter paper. Wash the precipitate back into the beaker, using as little water as possible, and dissolve any precipitate that remains strongly adherent with a few drops of caustic soda solution. Add about 20 grms. of solid

sodium hydrate, and when this is dissolved, about 6 c.c. of bromine, and digest on the water-bath till all the sulphur is oxidized. Add a drop of hydrochloric acid. If bromine vapour is given off, enough bromine has been added; if it be not, add a little more bromine and repeat the digestion. Boil for a few minutes, add alcohol to about $\frac{1}{2}$ the volume of the solution, and let stand for some hours, then filter, and wash.

Estimation of the Antimony.—Wash the precipitate back into the beaker, and dissolve in hot hydrochloric acid containing a little tartaric acid, dissolve any precipitate that remains adherent to the paper in the same mixture; and if any undissolved sulphur remains, filter it off, heat the solution to boiling, pass hydrogen sulphide to complete saturation. The antimony is precipitated as antimony sulphide, Sb_2S_3 , and may be converted into oxide and weighed, as directed on p. 300, or determined as follows:—

Let stand in a warm place till the odour of sulphuretted hydrogen has nearly disappeared. Filter on to a weighed filter paper, wash once or twice by decantation, then on the filter, dry at 100° , and weigh. The precipitate is antimony sulphide, containing some water and some free sulphur.

Weigh a porcelain boat, transfer a portion of the weighed precipitate to it, and weigh again; the increase in weight is the amount of precipitate taken. Place the boat in a short combustion tube over a large Bunsen burner, and pass a gentle stream of pure dry carbon dioxide; when the air has been displaced, heat gently till no more sulphur is given off and the residue has become black, then let cool in the stream of carbon dioxide, and weigh. The boat now contains pure antimony sulphide, and from the amount left it is easy to calculate the weight of antimony sulphide in the whole precipitate.

Estimation of the Tin.—Dilute the filtrate from the sodium antimoniate precipitate, add hydrochloric acid in slight excess, and warm till the odour of bromine disappears. Saturate with sulphuretted hydrogen, let stand till the precipitate settles, filter, and wash, adding some ammonium acetate to the wash-water should the precipitate show signs of passing through the paper. Dry, convert the tin sulphide into oxide as above, and weigh as SnO_2 .

Estimation of Lead, etc.—Dry the precipitate from the sodium sulphide precipitation, transfer it as completely as possible to a beaker, burn the filter paper, and add the ash. Moisten the residue with strong nitric acid, then cover with red fuming nitric acid, and warm till all the sulphur is oxidized. Add a little strong sulphuric acid, and evaporate till sulphuric acid is evolved. Cool, dilute slightly, filter off the precipitated lead sulphate, $PbSO_4$, and dry, ignite, and weigh.

The copper and other metals may be determined in the filtrate exactly as directed—Method I.

10. HARD LEAD.—This is essentially lead containing a considerable quantity of antimony, with smaller quantities of other metals.

Weigh out 1 grm. of the finely divided alloy, transfer to a small beaker, add about 2 grms. of tartaric acid, then nitric acid, sp. gr. 1.2, and warm till solution is complete; dilute, add sodium hydrate in excess, and either saturate with sulphuretted hydrogen or add some yellow sodium sulphide; cover and digest in a warm place for about an hour, filter, and wash well with water containing a little sodium sulphide.

Estimation of Antimony.—To the filtrate add hydrochloric acid in slight excess, let stand in a warm place for a short time, filter, wash with water containing sulphuretted hydrogen, and estimate the antimony as directed on p. 302.

Should tin be present—as is often the case—it may be separated as directed on p. 301.

Estimation of the Lead, etc.—Dry the sulphuretted hydrogen precipitate, transfer it to a small beaker, burn the filter paper, and add the ash; cover with strong nitric acid, and warm till solution is complete. Should globules of sulphur form, and resist oxidation, they may be picked out, burnt in a crucible, and the residue dissolved in a drop of nitric acid and returned to the beaker; add a little sulphuric acid, evaporate till nitric acid is removed, then dilute, add alcohol, let stand, filter, dry, ignite, and weigh the $PbSO_4$.

Estimation of Copper, etc.—The filtrate from the lead will contain the copper, etc. Boil off alcohol, and estimate the copper as directed for Brass (p. 293).

11. SPECULUM METAL.—This is an alloy of tin and copper, often containing arsenic. Weigh 1 grm., dissolve in a small quantity of aqua regia, dilute, add sodium hydrate in excess, then sodium sulphide, digest for two hours in a warm place, filter, wash once or twice by decantation, and repeat the digestion with ammonium sulphide; filter, wash well with water containing sodium sulphide, mix the filtrates.

Separation of the Arsenic and Tin.—Acidify the filtrate, let stand for some hours in a warm place, then filter, and wash. Transfer precipitated sulphide to a flask or retort fitted with a Liebig condenser; cover with strong hydrochloric acid, and warm, adding a drop or two of nitric acid to complete the solution. When solution is complete, add a considerable quantity of strong hydrochloric acid, in which some cuprous chloride has been dissolved, distil slowly for half an hour, receiving the distillate in water, then add a little more strong hydrochloric

acid and distil for another half hour. Change the receiver, add more hydrochloric acid, distil for about ten minutes. Then remove the receiver, and test the distillate with sulphuretted hydrogen. If no precipitate forms, the whole of the arsenic is over; but should one be produced, the receiver must be replaced, and the distillation continued.

Saturate the distillate with sulphuretted hydrogen, let stand in warm place for half an hour, filter on to a tared filter (p. 52), wash first with water, then with alcohol, and finally with carbon disulphide to remove free sulphur, dry at 100° , and weigh as arsenious sulphide.

Or dissolve the arsenious sulphide in aqua regia, add ammonia in excess, then ammonium chloride, and precipitate the arsenic acid with magnesia mixture, and weigh (see p. 250).

Determination of Lead, Copper, etc.—Dissolve the precipitated sulphides in nitric acid, and proceed exactly as directed on p. 293.

12. PHOSPHOR TIN.—This is an alloy of tin and phosphorus made by fusing the two elements together. It is largely used in the manufacture of phosphor bronze and other alloys.

Weigh 1 grm. of the alloy in fine powder into a small flask, fitted with a cork and separator funnel and exit tube, add about 20 c.c. of water, then about 10 c.c. of bromine in small portions at a time from the funnel. The flask should be placed in cold water, as the action must not be too rapid, and rise of temperature must be avoided. If small portions of the substance remain unattacked, more bromine must be added. Heat the mixture gently in the water-bath, and then allow it to stand for some time. Transfer the solution to a beaker, rinse the flask with strong hydrochloric acid, which will dissolve any separated stannic oxide, and heat gently till all bromine is expelled.

Separation of Tin.—Add ammonia in slight excess, then ammonium sulphide, and warm till the tin sulphide is dissolved, then filter and wash with water containing ammonium sulphide.

Lead, Copper, etc.—Estimate the lead, copper, etc., in the precipitate as directed on p. 303.

Estimation of Tin.—Acidify the filtrate with hydrochloric acid, let stand in a warm place, filter, wash the precipitated tin sulphide with water containing ammonium acetate, dry, and estimate as SnO_2 , as directed on p. 300.

Estimation of Phosphorus.—Evaporate the filtrate from the tin sulphide to small bulk, filter off any sulphur that separates, add ammonia in excess, then magnesia mixture, stir vigorously, let stand some hours, filter, wash, dry, ignite, and weigh as magnesium pyrophosphate (p. 358).

12a.—Where it is only required to estimate the phosphorus, the following short method may be used.

Dissolve exactly as directed in 12, and proceed as far as the expulsion of the bromine. Transfer the solution to a litre flask, dilute to somewhat less than a litre, and saturate with sulphuretted hydrogen. Let stand in a warm place for some time, dilute to the mark, shake up well, then let settle. Filter 500 c.c. through a dry paper, evaporate the solution to small bulk, and determine the phosphorus as magnesium pyrophosphate as before. An error is of course introduced by the presence of the solid tin sulphide, but in the bulk of solution given this is very small, and may be neglected.

13. FUSIBLE METAL.—Fusible metal usually contains tin, lead, and bismuth, and frequently cadmium, and traces of other metals.

Method 1.—Dissolve 1 grm. of the alloy, as finely divided as possible in 15 c.c. aqua regia, heat till excess of acid is expelled, and dilute. No notice need be taken of oxychloride of bismuth, which may be precipitated. Add sodium hydrate in excess, then yellow sodium sulphide, stir, and stand aside in a warm place for some hours. Filter on to a tared filter as rapidly as possible, and wash with water containing ammonium sulphide.

Estimation of the Tin.—Acidify the filtrate with hydrochloric acid ; let stand in a warm place, filter, wash, dry, calcine, and weigh the tin oxide as directed on p. 300.

Separation of Bismuth.—Dry the filter with the precipitated sulphides at 100° till the loss of weight, after fifteen minutes' heating, is small. Filtration and drying must be conducted as rapidly as possible to avoid oxidation.

Transfer the dry precipitate to an agate mortar ; powder it, transfer a portion to a porcelain boat, weigh, and cover with pure sulphur. Put the boat into the tube of an apparatus, similar to Fig. 80, but so arranged that a stream of air saturated with bromine can be sent through it. Pass a stream of dry air through the tube, warming very gently. When no more moisture seems to be expelled, connect the bromine, and pass a rapid stream of air laden with bromine, passing the escaping gas into very dilute nitric acid. Warm gently with a Bunsen burner, held in the hand and kept moving, but do not heat strongly. The operation should be complete in about half an hour.

Estimation of the Bismuth.—Evaporate the nitric acid solution to small bulk, adding more nitric acid, should basic salts precipitate. Whilst still hot, add ammonia in excess ; then ammonium carbonate ; boil, filter, wash, dry, ignite, and weigh the bismuth oxide. Again cover with ammonium carbonate ; heat gently till all ammonium carbonate is expelled, weigh, and repeat, till the weight is constant. Factor $\text{Bi} = 0.89767$.

Separation and Estimation of Lead.—Transfer the residue in the boat to a small beaker, cover with strong nitric acid, and warm till oxidation is complete. Remove the boat and wash, then add sulphuric acid, evaporate till the nitric acid is expelled, cool, dilute, add alcohol, let stand, filter, dry, ignite, and weigh the lead as sulphate (*see* Lead).

Estimation of Cadmium.—Dilute the filtrate from the lead sulphate precipitate and saturate with sulphuretted hydrogen, let stand till the precipitate has subsided, then pipette or decant off some of the clear solution, dilute it further, and saturate with sulphuretted hydrogen. Should no further precipitate fall, precipitation may be taken as being complete, but should there be a further precipitate, return the portion to the original beaker, dilute, saturate with hydrogen sulphide, and so on till precipitation is found to be complete, then filter, wash with water containing sulphuretted hydrogen, dry at 100° , and weigh. Should the precipitate be suspected to contain free sulphur, after drying, wash once or twice with carbon disulphide till a drop of the filtrate leaves no residue on evaporation. Filter carbon disulphide through a paper wetted with it.

Method 2.—The solution and removal of the tin are effected as directed above by aqua regia and sodium sulphide. The precipitate containing bismuth, lead, and cadmium, is dissolved in dilute nitric acid, and evaporated with hydrochloric acid nearly to dryness, care being taken to completely dissolve sulphur. To the solution a few drops of strong hydrochloric acid are added to prevent precipitation of the bismuth on dilution.

Dilute sulphuric acid is then added and well shaken, followed by the addition of alcohol in quantity equal to the bulk of the solution. After standing to deposit the lead sulphate, the precipitate is filtered and washed, first with dilute alcohol, containing a little hydrochloric acid, and finally with strong alcohol. The precipitated lead sulphate is dealt with as previously described.

The bismuth is determined by boiling off the alcohol, diluting largely, and filtering the oxychloride precipitated. This may be dissolved in hydrochloric acid, ammonia added in excess, and the precipitated hydrate filtered, washed, dried, ignited with ammonium carbonate, and weighed as Bi_2O_3 .

Bismuth may also be estimated by precipitation with lead, as described on p. 266.

Cadmium is estimated in the filtrate from bismuth as previously described.

SILVER ALLOYS.

14. Silver alloys usually contain only silver and copper, with traces of other metals derived from the copper used.

Method 1.—Weigh 1 grm. of the alloy, and dissolve it in nitric acid, free from chlorine.

Determination of Silver.—Heat the solution to boiling, and add hydrochloric acid drop by drop till precipitation is complete. Decant through a filter and redissolve the precipitate in ammonia, in the beaker in which precipitation took place, dilute, boil off most of the ammonia, then add nitric acid in excess, boil and filter, wash, and dry. The precipitate is removed as completely as possible from the filter paper, the filter paper is burned, the ash collected on the lid of the crucible, moistened with nitric acid, warmed, a drop of hydrochloric acid added, and then gently heated till all acid is expelled. The lid is then put on the crucible in an inverted position, the precipitate gently ignited, and weighed.

Estimation of the Copper.—The filtrate from the silver chloride contains the copper. Saturate with sulphuretted hydrogen, let stand in a warm place, filter, wash with sulphuretted hydrogen water, dry, convert into cuprous sulphide by heating with sulphur, as on p. 88, and weigh. If lead is present it must be separated by treatment with sulphuric acid and evaporation, and iron, etc., may be estimated in the filtrate. Or the copper may be estimated by other methods given (see Copper).

Method 2.—Determine the silver by dry assay (p. 117), or volumetrically (p. 129), and estimate the copper as above.

15. **GOLD ALLOYS.**—The gold and silver are best determined by dry assay, as directed on p. 147.

Estimation of other Metals.—(1) The alloy contains less than 25 per cent. of gold. Weigh out about 0.5 to 1 grm. of the alloy in as fine a state of division as possible, and boil with nitric acid, 1.2 sp. gr. in a parting flask, dilute, decant, leaving the residue of gold, and wash by decantation. Add more nitric acid, boil up again, filter, wash by decantation, and repeat this until a drop of the solution gives no precipitate with hydrochloric acid.

The gold may be transferred to a small gold annealing crucible heated to redness, and weighed on a watch-glass, or, after cupellation, as a prill.

Estimation of Silver, etc.—To the solution, from the gold, add hydrochloric acid to precipitate the silver, and estimate it as chloride, as directed on p. 307.

Estimation of Copper, Iron, etc.—Precipitate the copper with sulphuretted hydrogen, and weigh as subsulphide (p. 88). In the filtrate determine the iron as oxide by precipitation with ammonia (p. 172).

(2) The alloy contains more than 25 per cent. gold. The gold and silver may be determined by dry assay (see p. 148). Or weigh out from 0.5 or 1 gm. of the alloy, and treat with aqua regia. When solution seems to be complete, dilute with water, filter, wash by decantation, then on the filter; dissolve the silver chloride in ammonia, and should there be any black or metallic residue, return it to the beaker, add more aqua regia, and boil. Filter off, and wash any silver chloride, dissolve it in ammonia, and add it to the main ammoniacal solution.

Estimation of the Silver.—Acidify the ammoniacal solution with hydrochloric acid, and boil, filter, wash, ignite, and weigh the silver chloride, as directed on p. 307. Factor for Ag = 0.75271.

Separation of Platinum.—Mix the aqua regia solution and the filtrate from the silver chloride precipitate, and evaporate to small bulk. Transfer to a porcelain basin, evaporate the solution almost to dryness, add just enough water to dissolve most of the ammonium salts, then alcohol in excess. Let stand 12 hours, filter, wash with water containing a little ammonium chloride, dry, ignite, and weigh the precipitate, as metallic platinum.

Estimation of the Gold.—To the filtrate, from the platinum, after boiling to expel alcohol, or, in the absence of platinum, the evaporated filtrate from the silver chloride, add oxalic acid in considerable excess, and let stand in a warm place for 12 hours. Filter off the precipitate, dry, ignite in a porcelain crucible, and weigh as metal. Or collect as directed on p. 145, dry, ignite, and weigh.

Estimation of Lead and Copper.—To the filtrate, from the gold, add a little hydrochloric acid, and saturate with sulphuretted hydrogen. Filter off the precipitated copper and lead sulphides, wash, dry, dissolve in a small quantity of nitric acid, separate the lead as sulphate with sulphuric acid, and estimate the copper in the filtrate, either volumetrically (p. 85), or gravimetrically, as on p. 87. (*See Copper.*)

Estimation of the Iron.—To the filtrate, from the sulphide precipitate, add ammonia in slight excess, then a drop or two of ammonium sulphide, and warm, filter, wash the precipitate with water containing ammonium sulphide, dissolve it in hydrochloric acid, add a little nitric acid, boil, precipitate with ammonia, and filter. Ignite, and weigh as ferric oxide. Factor for Fe = 0.7.

ANALYSIS OF COMMERCIAL COPPER.

COMMERCIAL copper is never pure, though the purest forms, as electrotype copper and Lake Superior copper, contain but traces of impurities. All or any of the following impurities may be present, and must be looked for :—

Arsenic, Antimony, Lead, Bismuth, Tin, Iron, Nickel, Cobalt, Silver, Phosphorus, Sulphur, Oxygen as cuprous oxide.

As these impurities are only present in small quantity, it is best to use a separate portion for the determination of each of the constituents ; those bracketed may be determined in the same portions.

Copper.—Copper is best determined volumetrically by the iodide of potassium and thiosulphate method (p. 85), using portions of 0.5 grm. for each determination.

Tin.—Tin is rarely present in estimateable quantity. Dissolve 10 grms. of the copper, preferably in turnings, in nitric acid, evaporate off the excess of acid, and dilute. Should a residue remain, filter, dry, ignite, and weigh. It may be antimony or tin. Transfer it to a silver dish, and separate the antimony and tin by fusion with caustic soda (p. 299).

It is only in the rarest cases that the quantity will be large enough to allow of this separation. Where there is any large quantity of tin it is best treated as directed under Bronze (p. 294).

Arsenic and Antimony.—Dissolve 10 grms. of the metal in nitric acid, in a large beaker (No. 8), and dilute with cold water to about 750 c.c. Put into a small beaker a solution of ferric chloride, containing about 0.5 grm. of iron, and neutralize it as completely as possible with sodium carbonate.

To the cold copper solution add sodium carbonate, in small quantities at a time, till a permanent precipitate just forms. Dissolve this precipitate in the smallest possible quantity of hydrochloric acid, then add the neutralized ferric chloride solution, and heat. To the hot solution add a concentrated solution of sodium acetate, containing about 10 grms. of the salt, and heat to boiling. As soon as the solution actually boils, remove the burner, let the precipitate settle, filter

through a large filter, wash once or twice by decantation, then on the filter, till the washings are free from copper. The precipitate should be red basic acetate and arsenate of iron. Should it be pale buff it must be rejected, and a restart made, more iron being added; should it be dirty greenish, from the presence of copper, it must also be rejected. The presence of basic acetate of copper is usually due to insufficient free acid or long boiling.

Dissolve the precipitate in 10 c.c. hydrochloric acid, neutralize with ammonia, then add ammonium sulphide in excess (till the solution is yellow), digest in a warm place for half an hour, filter and wash. The precipitate of iron sulphide may be rejected. Acidify the filtrate with hydrochloric acid, let stand in a warm place for half an hour, and filter through a small filter. The precipitate contains the arsenic as As_2S_3 , and the antimony as Sb_2S_3 .

Transfer the precipitate, with the paper, to a small beaker, cover with aqua regia, warm till solution is complete, dilute, filter, and wash, using as little water as possible, so that the total bulk does not much exceed 20 c.c., add ammonia in excess—the solution should remain perfectly clear—then magnesia mixture, stir vigorously, let stand 12 hours, collect on a tared filter, wash with ammonia water, using as little as possible, dry at 100°C ., and weigh. A mark must be put on the beaker indicating the height of the solution before filtering. This volume must be afterwards measured and 0.001 grm. added to the weight of the precipitate for each 10 c.c. of solution.

Should the ammoniacal solution not be quite clear, it must be acidified with hydrochloric acid, a crystal of tartaric acid added, and then the arsenic precipitated as above. As the arsenate precipitate may be contaminated with ammonium tartrate, it must be dissolved in hydrochloric acid, reprecipitated by ammonia, and treated as above.

The filtrate from the magnesium ammonium arsenate precipitate contains the antimony. Add to it a drop or two of ammonium sulphide. Should a small quantity of black precipitate of iron sulphide form, filter it off, and acidify the filtrate or the solution with hydrochloric acid, stand aside for a short time in a warm place, filter, wash, and dry. Transfer the precipitate as completely as possible to a porcelain crucible, cover with strong nitric acid, add red fuming acid, warm till all the sulphur is oxidized, then evaporate to dryness, dry, ignite, and weigh as antimony tetroxide (see p. 300). Factor for Sb = 0.7922.

The amount of arsenic may vary from 0.01 to 0.5, or more in exceptional cases, and the antimony from about a small trace to 0.1.

Abel and Field's Method.—Dissolve 10 grms. of the copper in nitric acid, add a quantity of lead nitrate solution containing about

5 grms. of the salt, then a solution of ammonia and carbonate of ammonia in excess. Let stand some hours, filter, wash the precipitate into a beaker, add 20 grms. of oxalic acid, dilute, boil, and stand in a warm place for half an hour. Filter, and wash. Add ammonia in slight excess to the filtrate, then saturate with hydrogen sulphide, and stand in a warm place for some time, filter off any precipitated copper or iron sulphide, acidify the filtrate with hydrochloric acid, and let stand in a warm place. Filter off the precipitated sulphides of arsenic and antimony, and separate and determine them as directed above.

Clarke's Method for Arsenic.—Weigh 10 grms. of the copper in the form of shot, drillings, or turnings. Transfer to a flask (see p. 303), cover with a strong hydrochloric acid solution of ferric or cupric chloride, containing about 10 grms. of iron or copper, and heat gently till solution is complete, which may occupy about one hour; then add 25 c.c. of strong hydrochloric acid and distil for half an hour; then add more hydrochloric acid, change the receiver, and distil again, and so on till the distillate is free from arsenic.

The arsenic in the distillate is precipitated as sulphide by sulphuretted hydrogen, and may either be weighed as such, or converted into magnesium ammonium arsenate, as above.

Lead and Bismuth.—Abel and Field's Method.—Dissolve 10 grms. of the metal in nitric acid in a large beaker, and heat, add about 1 gm. of sodium phosphate, then ammonia in excess, and let stand for some hours, filter and wash thoroughly with dilute ammonia; dissolve the precipitate in hydrochloric acid, make alkaline with ammonia, and precipitate the lead and bismuth as sulphides by means of sulphuretted hydrogen, filter, and wash well; dissolve the precipitate in nitric acid, nearly neutralize with ammonia, add a small quantity of hydrated oxide or basic nitrate of copper, let stand for some time, then filter, and wash. The bismuth will be precipitated, but the lead will remain in solution. Dissolve the precipitate in nitric acid, add ammonia in excess, heat to boiling, filter off the bismuth hydrate, redissolve this in hydrochloric acid, pass sulphuretted hydrogen to separate the bismuth as sulphide from iron, filter, and wash. Dissolve the precipitate in a small quantity of nitric acid, add ammonia in excess, boil, filter, wash, dry, ignite, and weigh the Bi_2O_3 . To the filtrate from the copper-bismuth precipitate add sodium carbonate in excess, then acetic acid till the precipitate redissolves, and a little potassium chromate. The lead will be precipitated as chromate. Filter on to a tared filter, wash, dry at 100°C. , and weigh the PbCrO_4 . Factor $\text{Pb} = 0.63972$.

Method 2.—Weigh 10 grms. of the copper, dissolve it in nitric acid, precipitate the lead and bismuth as phosphate, as above, filter, and wash with ammonia water; dissolve the precipitate in a small quantity of hot nitric acid in a small beaker, evaporate till lead nitrate begins to crystallize, then take up with hot water, add a few drops sulphuric acid and alcohol, to about double the bulk of the solution, let stand for some hours, filter, wash first with sulphuric acid water, then with alcohol water, dry, ignite, and weigh the lead sulphate.

Boil the filtrate from the lead sulphate till alcohol is all expelled, then add ammonia in excess, and pass sulphuretted hydrogen, filter and wash, dissolve the precipitate in aqua regia, containing only a small quantity of nitric acid, dilute, saturate with hydrogen sulphide, filter, wash; dissolve the precipitate in nitric acid, add ammonia in excess, boil, filter, wash, dry, ignite, and weigh as bismuth oxide.

Method 3.—Dissolve 10 grms. of the copper in nitric acid, dilute considerably, add ammonium carbonate, then ammonia in excess, let stand for 12 hours, filter, and wash with ammonia water; dissolve the precipitate in hydrochloric acid, dilute, and saturate with sulphuretted hydrogen, filter, wash, and dry, transfer the precipitate to a small beaker, burn the paper, and add the ash, cover with strong nitric acid, and warm; as soon as solution is complete dilute a little, add some sulphuric acid and alcohol, and let stand for some hours, filter, wash with sulphuric acid water, then with alcohol and water, dry, ignite, and weigh the lead sulphate. Factor for Pb = 0.68295.

Boil the filtrate from the lead sulphate till alcohol is expelled, add a crystal of chlorate of potash, to destroy organic matter, and determine the bismuth as in Method 2.

Iron.—Dissolve 10 grms. of the copper in nitric acid, dilute, heat to boiling, add ammonia in excess, boil, and filter; dissolve the precipitate in hydrochloric acid, dilute, and saturate with sulphuretted hydrogen, let stand for a short time, filter, and wash. Boil the filtrate till sulphuretted hydrogen is all expelled. Add enough nitric acid to peroxidize the iron, then add ammonia in excess, boil, filter, wash, dry, ignite, and weigh the ferric oxide.

Nickel, Cobalt, and Zinc.—Nickel is often present, cobalt and zinc only rarely so. Dissolve 10 grms. of the copper in aqua regia, and evaporate till the nitric acid is nearly all expelled; dilute considerably, saturate with sulphuretted hydrogen, filter, and wash. Wash the precipitate back into the beaker, redissolve in aqua regia, boil off excess of nitric acid, and reprecipitate the copper with sulphuretted hydrogen. Mix the filtrates, boil till sulphuretted hydrogen is expelled, and evaporate to about 150 c.c. Add a little strong nitric acid to peroxidize

the iron, then add ammonia in excess, boil, and filter. Dissolve the precipitate in hydrochloric acid, and reprecipitate with ammonia. Repeat this solution and reprecipitation with ammonia at least twice. Mix the three filtrates, boil till ammonia is almost expelled, the solution remaining alkaline; then, while still boiling, saturate with sulphuretted hydrogen, filter, and wash with water containing sulphuretted hydrogen.

(*a*) **The only Metal present is Nickel.**—Dissolve the precipitated sulphide in aqua regia. Should sulphur separate, remove and burn it, adding the ash to the acid solution in the beaker, then add caustic soda in excess, boil, filter, dry, ignite, and weigh the nickel oxide NiO .

(*β*) **Nickel and Cobalt are present.**—Dissolve the precipitate as above, precipitate with caustic soda, filter and dry the precipitate. Transfer the dried precipitate to a weighed porcelain boat, burn the filter paper, and add the ash. Put the boat into a tube, pass a gentle current of hydrogen, heat to redness for fifteen minutes, cool in hydrogen, weigh the boat with the nickel and cobalt, dissolve the metals in aqua regia, and separate the cobalt with potassium nitrite, as directed on p. 195.

Or dissolve the precipitated sulphides in aqua regia, separate the cobalt as directed (p. 195), and estimate the nickel in the filtrate by adding ammonia in excess, precipitating the nickel as sulphide by sulphuretted hydrogen and estimating the nickel as in *a*.

(*γ*) **Zinc is, or may be, present.**—Dissolve the precipitated sulphides in aqua regia, evaporate excess of acid, neutralize with carbonate of soda, add a drop or two of acetic acid, so as to give a distinctly acid reaction, and saturate the *cold* solution with sulphuretted hydrogen, then add a few drops of sodium acetate solution and let stand twelve hours. The zinc will be precipitated. Filter, and wash with hydrogen sulphide water. Dissolve the precipitate in hydrochloric acid, precipitate with sodium carbonate. Boil, filter, dry, ignite strongly, and weigh as ZnO . Estimate the nickel and cobalt in the filtrate as above.

Silver.—Method 1.—Dissolve 10 grms. of the copper in nitric acid, and evaporate till any large excess of acid is expelled, dilute considerably, and add one or two drops of hydrochloric acid, let stand twelve hours, filter, wash, dry, ignite, and weigh the silver chloride.

Method 2.—Dissolve 10 grms. of the copper in nitric acid, as above, add 10 grms. of lead nitrate, then hydrochloric acid till no further precipitate forms. Filter, and wash the precipitate once or twice with cold water, transfer to a clay crucible, mix with 20 grms. of sodium carbonate, and 2 grms. of argol, and fuse in a wind furnace. Cupel the resulting lead (see p. 96), and weigh the silver.

Phosphorus.—Dissolve 10 grms. of the copper in aqua regia, add iron as ferric chloride, and precipitate with sodium acetate, exactly as directed on p. 309, for arsenic. Dissolve the precipitated basic acetate, phosphate, etc., in hydrochloric acid, add ammonia in excess, and saturate with sulphuretted hydrogen, or add ammonium sulphide, digest in a warm place for half an hour, filter, and wash well. Acidify the filtrate with hydrochloric acid to precipitate the arsenic, let stand in a warm place for half an hour, filter, and wash. Evaporate the filtrate containing the phosphorus as phosphoric acid to very small bulk, add ammonia in excess, then magnesia mixture, stir vigorously, let stand, filter, and wash with water containing a little ammonia, dry, ignite, and weigh the magnesium pyrophosphate. If the copper contains tin, the phosphorus may be estimated as directed for phosphor bronze (p. 296).

Sulphur.—Weigh 10 grms. of the copper, dissolve it in a mixture of 1 part nitric acid, 4 parts hydrochloric acid, and evaporate till all nitric acid is expelled, then dilute considerably, and nearly neutralize with ammonia, add a small quantity of barium chloride, heat to boiling, and let stand overnight, filter, wash, dry, ignite, and weigh the barium sulphate. Factor for S = 0.13748.

Oxygen—Cuprous Oxide.—This is almost invariably present in small but variable quantities, and has a great influence on the quality of the copper. It is, however, difficult, if not impossible, to estimate it accurately.

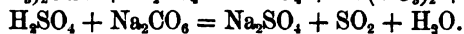
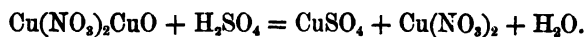
One method that has been suggested is to heat a finely divided sample of the metal to redness in a stream of hydrogen, and weigh the resulting water. The results obtained are rarely concordant, and it is not certain that the gain in weight of the drying tube is all water from the oxide.

Abel has suggested a method for determining oxygen in copper, which depends on the reduction of silver nitrate by cuprous oxide in presence of sulphuric acid. He "takes 5 grms. of the copper to be tested, previously reduced by proper mechanical means to powder or filings, and adds to it 1.3 grms. of solid silver nitrate, mixed in a mortar with 10 c.c. of dilute sulphuric acid. The decomposition sets in at once, and is complete after two hours' time; water is then added, the metallic silver is collected on a filter, well washed, and, after having been dried, is weighed."



The amount of oxide present may be calculated from the diminution of the quantity of silver precipitated by the copper. Or the copper oxide

present in the precipitate may be determined by carefully washing it, then digesting with 25 c.c. standard sulphuric acid (normal) at 50° C. for an hour, and titrating the excess of acid by normal sodium carbonate in the boiling solution till a faint cloudiness appears. The reaction is—



Since 143 parts of Cu_2O neutralize 98 of H_2SO_4 , the oxide may be calculated from the acid consumed.

The accuracy of the method is doubtful.

DETERMINATION OF IMPURITIES IN BRASS AND BRONZE.

THE impurities present in small quantity may be estimated exactly in the same manner as in pure copper, the metastannic acid being filtered off before each determination, except as regards the determination of arsenic and antimony when the alloy contains tin, and nickel and cobalt when it contains zinc.

Arsenic and Antimony.—(1) The quantity of antimony is very small, *i.e.* only that due to impurities in the metals used. Dissolve 10 grms. of the metal in the least possible quantity of aqua regia, dilute and pour into a solution of 25 grms. of caustic soda in water, then add yellow sodium sulphide, and digest in a warm place for an hour, filter, wash the precipitate into a basin, and repeat the digestion, filter, and again digest, finally filter, and wash. The precipitate may be rejected. Mix the filtrates and acidify with hydrochloric acid, let stand in a warm place, filter, wash, and dry the precipitate. Dissolve the precipitate in strong hydrochloric acid, adding a little nitric acid from time to time till solution is complete, filter off any separated sulphur, dilute to 200 c.c., then add 25 grms. of oxalic acid, heat to boiling, and pass a rapid current of sulphuretted hydrogen for twenty minutes. Antimony and arsenic are precipitated as sulphides, tin remaining in solution. Let stand for half an hour, pass a bubble or two more sulphuretted hydrogen, then filter, and wash with sulphuretted hydrogen water. Dissolve the precipitate in ammonium sulphide, reprecipitate with a strong solution of oxalic acid, boil, pass sulphuretted hydrogen, let stand in a warm place, and filter. Dissolve the precipitate in aqua regia (see p. 310), add a few crystals of tartaric acid, make alkaline, and precipitate the arsenic with magnesia mixture. Let stand twelve hours, filter, redissolve the precipitate in hydrochloric acid, add ammonia in excess, stir well, filter on to a tared filter, wash with ammonia water, dry at 100°, and weigh as ammonio-magnesium arsenate. Through the filtrate from the first precipitation of the arsenic pass sulphuretted hydrogen, let stand half an hour, filter off the antimony sulphide, dry, transfer to a crucible, heat with strong (1.5 sp. gr.) HNO_3 , ignite, and weigh as antimony tetroxide (see p. 300).

(2) The amount of antimony is considerable. Dissolve the alloy in aqua regia, using as little nitric acid as possible, and boil till all nitric acid is expelled; add some potassium metabisulphite, to reduce the salts present as far as possible, then add strong hydrochloric acid and some cuprous chloride, and separate the arsenic by distillation, as directed on p. 303.

Dilute the residue in the flask, and separate the tin and antimony by repeated digestion with sodium sulphide as above. Precipitate the sulphides with hydrochloric acid, and either (1) separate the antimony exactly as directed above, omitting the separation of the arsenic, or (2) oxidize the sulphides to oxides with strong nitric acid, treat with strong solution of caustic soda or by fusion, and separate as directed on p. 300.

Estimation of Nickel.—Determine the zinc, together with the small quantity of nickel, as directed on p. 292.

(1) The quantity of zinc present is considerable, say over 10 per cent.

Dissolve 10 grms. of the metal in aqua regia, and separate the copper as sulphide, as directed for copper on p. 312, boil off sulphuretted hydrogen, transfer the solution to a porcelain dish, add caustic soda in excess, boil, and filter.

The precipitate will contain nickel and cobalt, with some zinc and iron.

(a) Dissolve the precipitate in hydrochloric acid, nearly neutralize with ammonia, add about 1 grm. of sodium formate, and dilute to about 300 c.c., then add 3 c.c. of formic acid, sp. gr. 1.2, heat to 50° C., saturate with sulphuretted hydrogen, filter at once, and wash with water containing sulphuretted hydrogen. The precipitate will contain all the zinc.

Add to the filtrate a little hydrochloric acid, and boil till all sulphuretted hydrogen is expelled; then add ammonia in excess, boil, and filter off the iron, redissolving and reprecipitating to remove the last traces of nickel. To the filtrate add a considerable quantity of nitric acid, and evaporate till ammonium salts are expelled, adding more nitric acid from time to time as may be necessary. Then precipitate the nickel with sodium hydrate, and weigh as nickel oxide.

(b) Dry the sodium hydrate precipitate, transfer it to a porcelain crucible, burn the paper, and add the ash; add about a gramme of pure charcoal, made from sugar, bed the crucible in magnesia, or lime, or in a large clay crucible, and heat very strongly in a wind furnace for one hour. Let cool, boil the carbonaceous residue with aqua regia, filter, and in the solution separate the iron and determine the nickel as directed above.

(2) The quantity of zinc is small. The preliminary precipitation with sodium hydrate may be omitted, and either of the above methods followed.

COMMERCIAL ZINC (SPELTER, ZINC-SHEET, ETC.).

THE impurities likely to be present, and which must be looked for and estimated, are—

Tin, lead, iron, cadmium, copper, arsenic, and very rarely antimony.

Tin.—This metal is rarely present except in minute quantities. It is generally sufficient to dissolve 10 grms. of the metal in nitric acid, evaporate nearly to dryness, take up with nitric acid, dilute, filter, wash, dry, ignite, and weigh the tin oxide.

Lead.—Dissolve 10 grms. of the metal, in nitric acid, and proceed exactly as directed for the determination of lead in copper (p. 311).

Iron.—Dissolve 10 grms. of the metal, and proceed exactly as directed for the determination of iron in copper (p. 312).

Cadmium.—Dissolve 10 grms. of the zinc in nitro-hydrochloric acid, and evaporate till zinc chloride begins to crystallize, dilute to 250 c.c., add a few drops of hydrochloric acid, and saturate with sulphuretted hydrogen at 60° C., let stand, filter, and wash. The precipitate will contain the copper, lead, cadmium, and a little zinc. Dissolve the precipitate in hydrochloric acid, with addition of a little nitric acid; evaporate off excess of acid, dilute as before, and repeat the precipitation with sulphuretted hydrogen. The precipitate should now be free from zinc. Dissolve in nitro-hydrochloric acid, dilute, add carbonate of soda to slight excess, then a solution of pure potassium cyanide, and digest for an hour. Filter (the precipitate is lead carbonate), and wash. Saturate the filtrate with sulphuretted hydrogen, and let stand for some hours in a warm place. The cadmium will be precipitated as sulphide. Filter on to a tared filter, wash with sulphuretted hydrogen water, dry at 100°, and weigh as cadmium sulphide, CdS , or dissolve the precipitate in strong hydrochloric acid, dilute, precipitate with sodium carbonate, filter, wash, dry, ignite, and weigh as cadmium oxide.

Copper.—Dissolve 10 grms. of the metal, in aqua regia, boil off excess of acid, remove the lead by evaporation with sulphuric acid, dilute, filter, heat the filtrate to boiling, nearly neutralize, and add a few crystals of sodium thiosulphate till all the copper is precipitated, and the supernatant solution is white or milky. Filter,

dissolve the precipitate in nitric acid, and determine the copper volumetrically (p. 86), or evaporate to small bulk, and determine the copper as oxide or sulphide (p. 88). Or the lead may be removed from the original solution of the metal by evaporation with 10 c.c. of sulphuric acid, filtering off the lead sulphate. To the filtrate add 50 c.c. of strong sulphuric acid, and dilute to a litre. Precipitate the copper and cadmium by sulphuretted hydrogen, dissolve the precipitate, and deal with it as described above.

Arsenic.—(1) In absence of tin, take 10 grms. of the metal, and proceed exactly as for copper (p. 309).

(2) In presence of tin, proceed as directed for speculum metal (distillation process), p. 303.

(3) Weigh 10 grms. of the metal, transfer it to a flask fitted with a separator funnel and leading tube passing into nitrogen bulbs containing strong nitric acid. Cover the metal with water, and when connections are complete, cautiously add strong hydrochloric acid from the funnel, regulating the acid so as to produce a steady evolution of gas. The evolved gas contains the arsenic as arseniuretted hydrogen, which is oxidized by the nitric acid to arsenic acid. When solution is complete, aspirate a current of air through the apparatus, so as to displace the hydrogen. Rinse the contents of the bulbs into a beaker, boil off excess of acid, dilute somewhat, add ammonia in excess, then magnesia mixture, stir, let stand, filter on to a tared filter, wash with ammonia water, dry at 100°, and weigh (see p. 310).

COMMERCIAL TIN.

THE impurities likely to be present are—

Lead, arsenic, antimony, iron, manganese, copper, zinc, and occasionally traces of other metals.

Lead, Copper, Iron, Manganese, and Zinc.—Dissolve 10 grms. of the metal in hydrochloric acid, adding a few drops of nitric acid to assist solution. Then add sodium hydrate in excess and sodium sulphide (both of which must be free from iron), digest in a warm place, filter, and wash with weak sodium sulphide solution.

Estimation of Lead.—Dissolve the precipitate in strong nitric acid, add a little sulphuric acid, evaporate to small bulk, dilute, filter, wash and weigh the lead sulphate (p. 63).

Estimation of Copper.—Saturate the filtrate from the lead sulphate precipitate with sulphuretted hydrogen; filter, wash, and dry the precipitate, mix it with sulphur, ignite in hydrogen, and weigh as cuprous sulphide (p. 88).

Estimation of Iron.—Boil the filtrate from the copper sulphide precipitate till sulphuretted hydrogen is expelled, then add a little nitric acid to peroxidize the iron, precipitate with ammonia, filter, wash, redissolve, and reprecipitate, at least twice, and mix the filtrates, dry, ignite, and weigh the ferric oxide.

Manganese.—Acidify the mixed filtrates with hydrochloric acid till just acid, then add solid carbonate of ammonia in excess. The manganese will be precipitated as carbonate; let stand in a warm place, filter through a double filter, wash with hot water, dry, ignite strongly, and weigh the manganese, Mn_2O_3 .

Estimation of Zinc.—In the filtrate from the manganese estimate the zinc by precipitation as sulphide, as directed on p. 292.

Arsenic and Antimony.—Dissolve 10 grms. of the metal in aqua regia, separate the arsenic by distillation with cuprous chloride, as directed on p. 303.

From the solution separate the copper by means of sodium hydrate and sodium sulphide as above, and separate the antimony by hydrogen sulphide and oxalic acid, as directed on p. 316.

COMMERCIAL NICKEL.

COMMERCIAL nickel comes into the market in two forms—cast and granulated nickel and cube nickel, the latter being the less pure, and frequently containing intermixed carbon.

The impurities which must be looked for, and, if present, estimated, are copper, tin, iron, cobalt, silicon, carbon, arsenic, antimony, and sulphur.

Silicon, etc.—Dissolve 10 grms. of the metal in aqua regia, and evaporate to dryness, take up with hydrochloric acid, and again evaporate to dryness, then take up with hydrochloric acid, dilute, filter, wash, dry, and ignite, and weigh the silica, SiO_2 . Factor, $\text{Si} = 0.4672$.

Copper.—Dilute the filtrate from the silica, warm, saturate with sulphuretted hydrogen, and estimate copper in the precipitate, as directed on p. 293, or colorimetrically after separation (p. 89).

Iron.—Boil the filtrate from the sulphuretted hydrogen precipitate till all sulphuretted hydrogen is expelled, add nitric acid to peroxidize the iron, and precipitate with ammonia in excess. Dissolve the precipitate in hydrochloric acid, reprecipitate, and weigh the ferric oxide (p. 172). Mix the filtrates.

Cobalt.—Evaporate the mixed filtrates to small bulk, add strong nitric acid, and heat, then evaporate almost to dryness till ammonium salts and the excess of nitric acid are expelled, dilute sufficiently to keep all the nickel salts in solution, neutralize with caustic potash, and make distinctly acid with acetic acid. Make a concentrated solution of potassium nitrite, acidify it with acetic acid, and filter off any flocks of silica and alumina that may separate. Add a considerable quantity of this to the nickel solution. Let stand for 24 hours in a warm place. Take out a portion of the clear supernatant fluid with a pipette, mix with more of the nitrite solution, and let stand for some hours. If no precipitate forms, precipitation may be assumed to be complete; but if a precipitate falls, the portion must be returned to the beaker, more nitrite added, and after long standing the filtrate tested again, filter, wash with 10 per cent. solution of potassium acetate, containing

a little potassium nitrite, till all the nickel is removed, dry, burn the filter paper, and dissolve the precipitate and ash in hydrochloric acid in a porcelain basin, add sodium hydrate in excess, boil, filter, wash thoroughly with hot water, dry, transfer the precipitate to a crucible, burn the filter paper, and add the ash. Ignite in a stream of hydrogen till weight is constant, and weigh the metallic cobalt (see p. 195).

Carbon.—Dissolve 1 grm. of the metal in ammonium copper chloride, and proceed exactly as directed for iron (p. 335).

Arsenic and Antimony.—Proceed as directed for copper (p. 309).

Sulphur.—Proceed as directed for brass (p. 314).

Electrolytic Estimation of Nickel in Ferro Nickel.—Two and a half grammes of the metal is dissolved in 40 c.c. of aqua regia, and evaporated to dryness. The residue is taken up with 40 c.c. of dilute sulphuric acid (1 : 4), and evaporated to fuming point. The liquor is cooled and diluted to 50 c.c. with cold water, and heated till complete solution has taken place. The solution is then diluted to 150 c.c. copper precipitated by saturating with sulphuretted hydrogen, and the precipitate collected for estimation (see above). After washing the filter paper with dilute sulphuric acid, the filtrate is first boiled to completely expel sulphuretted hydrogen, cooled, and 2 or 3 c.c. of bromine added and allowed to dissolve. The solution is poured with constant stirring into about 50 to 75 c.c. of strong ammonia in a beaker, and digested for 10 minutes. The hydrates of iron and manganese which are precipitated are filtered off and washed. The filtrate and washings are diluted to 250 c.c., thoroughly mixed by shaking, and 50 c.c. measured out

$$= \frac{25}{5} = 0.5 \text{ grm. of original sample into a No. 5 evaporating basin,}$$

boiled till free ammonia is expelled, and then 40 c.c. of dilute sulphuric acid (1 : 4) added, and evaporated to fuming point. The residue is cautiously dissolved in cold water, and transferred to a beaker containing platinum electrodes (see Copper, p. 92), and made strongly alkaline with ammonia. The volume should not greatly exceed 50 c.c. The cathode having been previously weighed, the electro deposition is proceeded with. Two Bunsen's cells or four Daniell's cells, giving a current of from 3–4 volts, should be employed as the source of electricity. The deposition is conducted as for copper, and the temperature should not fall below 70° F. The removal of the nickel is complete when ammonium sulphide gives no black or brown tinge with a drop of the liquid on a white tile. Traces of nickel left in solution may be estimated colorimetrically, as for copper, but using colourless ammonium sulphide in place of ferrocyanide of potassium.

If a deep platinum dish is available, the deposition may be effected in it, using the dish as a cathode, connected to the Zn of the battery, and thus forming the negative electrode. The dish should rest on a metallic support of silver or platinum in connection with the battery, or may itself be provided with a binding screw for connection.

The precipitated nickel should be reguline and closely adherent. It is washed in water, then with alcohol, dried, and weighed.

The increase in weight multiplied by 200 gives the percentage present.

COMMERCIAL ALUMINIUM.

THE purity of aluminium varies very much. That now made is nearly pure, and often contains over 99.5 per cent. of aluminium. In many articles made of aluminium, small quantities of other metals are alloyed.

The constituents usually present are copper, iron, lead, silicon, carbon, alkalis, calcium, and magnesium. Bismuth, tin, and zinc are frequently added to aluminium.

Copper, Iron, etc.—Dissolve 10 grms. of the metal in hydrochloric acid, adding a few drops of nitric acid, if necessary, to complete solution. Filter if necessary. Saturate the warm solution with sulphuretted hydrogen, let stand, filter, wash with water containing sulphuretted hydrogen, and separate the copper and lead in the precipitate as directed on p. 303.

Iron.—Boil the filtrate from the copper precipitate till all sulphuretted hydrogen is expelled, then add a little nitric acid in excess, and evaporate to small bulk. Pour the solution with constant stirring into a strong hot solution of caustic soda (containing 50 grms. of the solid), which must be kept in excess, rinse the beaker, adding the rinsings to the soda, boil for a short time, then dilute, filter, and wash thoroughly, dissolve the residue in hydrochloric acid, add ammonia in excess, boil, filter, wash, dry, ignite, and weigh the ferric oxide.

Silicon.—Dissolve 10 grms. of the metal in aqua regia, evaporate to dryness, take up with hydrochloric acid, and again evaporate to dryness, take up with hydrochloric acid, dilute somewhat, filter, dry, ignite, and weigh the silica.

Alkalis.—Dissolve 10 grms. of the metal in aqua regia, dilute, and precipitate the iron and alumina by means of ammonia, filter, and wash. Dissolve the precipitate in nitric acid, evaporate to dryness over the water-bath, and heat till the aluminium nitrate is all decomposed. Add hot water, boil, filter, and mix the filtrate with that from the ammonia precipitate. Saturate the solution with hydrogen sulphide, filter, and wash. Add ammonium oxalate, boil, filter, and wash, dry, ignite, and weigh the calcium as lime, CaO . Evaporate the filtrate to small bulk.

add a little pure oxalic acid, evaporate to complete dryness, and ignite. Let cool, treat the residue with repeated small quantities of hot water decanting through a small filter, dry the filter, burn the filter paper, add the ash, and weigh the magnesia.

Add hydrochloric acid in excess to the solution, evaporate to small bulk. Transfer the solution to a weighed platinum crucible, evaporate to complete dryness on the water-bath, then ignite gently, and weigh the alkalies as chlorides. If it be desired to separate them, see p. 371. For factors, see Appendix.

COMMERCIAL LEAD.

COMMERCIAL lead is usually so pure that the impurities present are in such small quantities as to be almost inestimable. The only constituents which it is necessary to estimate are silver and zinc, the latter only being present when the lead has been desilverized by zinc.

Silver.—Estimate by cupellation (see p. 109).

Zinc.—Dissolve 10 grms. of the metal in dilute nitric acid, add sulphuric acid to precipitate the bulk of the lead, let stand some time, filter cold, and wash with cold water, dilute the filtrate considerably, and saturate with hydrogen sulphide to complete the removal of the lead, and any copper, antimony, etc., present. Let stand, filter, boil off all hydrogen sulphide, add ammonia in excess, and saturate with hydrogen sulphide. Filter, wash with ammonium sulphide water, remove as completely as possible to a porcelain crucible, ignite with free access of air, add ammonium carbonate, and ignite again, cool, and weigh as zinc oxide. Factor, $Zn = 0.80263$.

Arsenic and Antimony.—The determination of these metals may be effected in the manner prescribed for brass (p. 316), the bulk of the lead being removed by precipitation with sulphuric acid prior to pouring the solution into caustic soda.

ANALYSIS OF IRON ORES.

In the complete analysis of iron ores, the following determinations are required :—

Total iron : iron as Fe_2O_3 , and as FeO : manganese : silica, free and combined : phosphoric acid : sulphur : alumina : lime : magnesia : alkalis : carbonic acid : organic matter : moisture : loss on ignition : and combined water and organic matter. In special cases other metals may require determination.

Moisture.—Two grms. of the ore is dried in the water oven till the weight is constant. With blackband and pyritical ores this is difficult, and drying for one hour is sufficient.

Loss on Ignition.—Two grms. of the ore is ignited over a bunsen, and then for 5 minutes over a foot blow-pipe or in a muffle, till the weight is constant.

Combined Water and Organic Matter.—One grm. of the ore, dried at 100°C ., is placed in a porcelain boat, and ignited at a high temperature in pure dry oxygen in the apparatus used for burning the carbonaceous residue from steel (Fig. 88). The drying-tube must, however, be weighed as well as the potash bulbs, and the final aspiration continued till all water is carried over. The increase in weight of the drying-tube gives the combined water, plus that derived from combustion of hydrogen in the organic matter, and the increase in weight of the potash bulbs gives the carbon dioxide yielded by the organic matter, plus the carbon dioxide from the carbonates present. After estimating the latter, it is deducted from the total, and the carbon in the remainder, reported as carbon in organic matter.

The residue after this treatment must be examined for carbonates by the method given below. Any carbon dioxide found must be added to the increase in weight of the potash bulbs before deducting the carbon dioxide in carbonates.

It is also advisable to make a determination of combined water by heating 1 grm. of the dried ore in a current of dry carbon dioxide, generated from a Kipp's apparatus (see Fig. 80), the ore being gently heated, and the escaping gas passed through a weighed calcium chloride tube.

From the difference between the combined water and the water

obtained by heating in oxygen, the hydrogen present in the organic matter is obtained.

Estimation of Total Iron.—This may be effected by potassium bichromate, or permanganate (see pp. 176–182).

Notes.—It is desirable in the presence of Titanium, *e.g.* in clay ironstones and titaniferous iron ores and bauxites, to reduce the iron to the ferrous condition with sulphur dioxide. In most other cases reduction by stannous chloride in boiling solutions is the most satisfactory procedure. Most ores are soluble in hydrochloric acid or are completely decomposed by it. Such as are too refractory are best dealt with by fusion with acid potassium sulphate. One grm. of the ore is fused with 10 grms. of the salt for 25 minutes, extracted with water and sulphuric acid, and dealt with (without evaporation) in the usual manner.

With blackband ores evaporation with nitric acid or potassium chlorate is insufficient to destroy the organic matter, and it must be burnt off in a platinum dish over a bunsen, or in a muffle, prior to solution.

Estimation of Ferrous Oxide.—This is accomplished in carbonates, clay ironstones, and blackband ores by boiling 1 grm. of the ore with 50 c.c. strong hydrochloric acid in a flask fitted with a valve as for standardizing (see Fig. 73). Two grms. of pure carbonate of soda is introduced into the flask to expel the air prior to adding the ore.

After diluting with well-boiled water, the assay is titrated with standard potassium bichromate. This determination is carried out on calcined spathic ores, clay ironstones, blackband ores as a check on the thoroughness of the calcination, and on magnetites, tap cinder, Northampton and certain Spanish ores.

The results are interfered with by black oxide of manganese, MnO_2 , and by organic matter. In the former case the results are low, and in the latter high. It is not often, however, that ores containing MnO_2 are examined for ferrous oxide, and the latter difficulty may be largely overcome by rapid filtration, and washing with boiled water prior to titration. Unless rapidly done, the solution is best not filtered, or the ferrous salt will oxidize, and the result be low.

With insoluble ores, in estimating the FeO , the fusion with potassium hydrogen sulphate is carried out in an atmosphere of carbon dioxide, or preferably nitrogen, the dish in which fusion is effected being covered with a perforated clay cover, and a stream of the gas passed in by means of a clay tube. Or the method given on p. 181 may be used.

Estimation of Ferric Oxide.—This may be done direct by the method given (p. 178), or may be taken as the difference between the total iron and the ferrous iron determined as above.

Estimation of Total Manganese.—Five grms. of the ore is dissolved in 40 c.c. of strong hydrochloric acid, evaporated to dryness with 20 c.c. of strong nitric acid, and heated. If much organic matter be present, as in blackband ores, the sample must be previously calcined,

or KClO_4 , must be used during the evaporation to destroy it. The residue is moistened with hydrochloric acid and warmed, sufficient strong hydrochloric acid being used to dissolve it completely. After dilution to 50 c.c. the liquid is filtered, and the filter washed with hydrochloric acid and water. The manganese may then be estimated by Ford and Willans' method, or by the bromine method. In the former case the solution is first evaporated to small bulk—5 to 10 c.c.—50 c.c. of strong nitric acid added, and evaporated to half bulk to expel hydrochloric acid. The solution then contains the iron and manganese principally as nitrates, from which the manganese is precipitated as hydrated peroxide by the addition of about 15 grms. of pure potassium chlorate in 3 or 4 doses to the boiling solution. Further addition of strong nitric acid is made to replace that removed, as required. The precipitate is collected and treated as directed on p. 355.

By the bromine method the solution of the residue (from evaporation) in hydrochloric acid is diluted and filtered, and treated exactly as for steel (see p. 353).

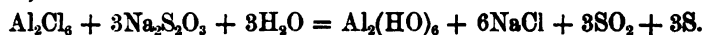
Determination of manganese existing as peroxide (see p. 203).

Silica and Insoluble Residue.—The insoluble residue from the manganese, after thorough washing, may be dried, ignited, and weighed as silica and insoluble, or 2 grms. of the ore may be specially treated with hydrochloric acid for this determination.

Alumina.—Two grms. of the ore is fused with pure acid sulphate of potash in a platinum dish, and the melted mass, after cooling, is extracted with water and hydrochloric acid in a large beaker. After washing and removing the platinum dish, the solution is evaporated to dryness with nitric acid, and the residue taken up with strong hydrochloric acid. It may then be diluted to 200 c.c. and the alumina determined by the phosphate method (see p. 362), or as follows:—

The filtrate containing the bases in solution is warmed, and the iron and aluminium precipitated as hydrates by cautiously adding ammonia in excess. The liquor is boiled for 10 minutes, and allowed to settle. The clear portion is decanted through a filter, and the precipitate is well washed by decantation. Any precipitate on the paper is washed back into the beaker, and the whole dissolved in the minimum amount of hydrochloric acid. The solution is diluted to 200 c.c., and the iron and alumina reprecipitated with ammonium acetate. To effect this, the solution is neutralized with ammonia, 40 grms. ammonium acetate added, and the solution heated just to boiling. The precipitate is filtered off and washed. (The combined filtrates, if mixed and evaporated, will serve for the determination of calcium, magnesium, and manganese.) The precipitate is dissolved in

hydrochloric acid, the iron reduced with potassium metabisulphite (cold), and the solution nearly neutralized with sodium carbonate. The alumina is then precipitated by adding sodium thiosulphate in excess, thus :—



After boiling till the sulphur dioxide has been expelled, the precipitate is filtered off, washed, dried, and ignited in a porcelain crucible with the lid removed, to burn off sulphur, and, after cooling, weighed, as Al_2O_3 .

Calcium and Magnesium.—The filtrate from the alumina and iron is made alkaline, if necessary, and treated with bromine for the separation of manganese, nickel, and copper exactly as described (page 353), or it may be treated with a little colourless ammonium sulphide or sulphuretted hydrogen passed through the boiling liquid. (The latter methods are tedious, owing to the slimy nature of the precipitate.) The precipitate of manganese, etc., is filtered off, and the calcium in the filtrate precipitated by adding oxalic acid followed by excess of ammonia, till the solution is distinctly alkaline. After boiling up, the precipitate is allowed to settle in a warm place for an hour or more. It is filtered (through a double paper if necessary), well washed with hot water, and, after drying, ignited very strongly, and weighed as CaO .



Magnesia.—The filtrate from the calcium oxalate is evaporated to small bulk, transferred to a conical flask fitted with a rubber stopper, and the magnesia precipitated as phosphate with ammonium phosphate. In doing this, it is best to acidify the solution with 2 to 5 c.c. hydrochloric acid, and, after adding the phosphate, to make strongly alkaline with ammonia. The liquid should be well shaken for 10 minutes and allowed to stand for some hours. The precipitate is filtered off, dried, ignited, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

Phosphorus and Arsenic.—These may be determined by the method given on p. 358 (Riley's method). Or, better, by a combination of the molybdate and magnesia methods. From 0.5 – 10 grms. of ore is taken, and, if soluble, dissolved in hydrochloric acid and nitric acid, evaporated to dryness, taken up with gentle heat by hydrochloric acid, diluted, the insoluble matter filtered off and washed, and the phosphoric acid determined as recommended for spiegeleisen and ferromanganese, with the omission of the addition of ferrous sulphate (p. 359).

They may also be determined by the direct molybdate method (p. 356).

Insoluble ores must be fused with 4 times their weight of a fusion mixture consisting of 2 parts sodium carbonate, 2 parts potassium carbonate, 1 part nitre. The melted mass is extracted with water and nitric acid, and the determination proceeded with by the molybdate and magnesia combined process.

Phosphorus only.—The ore is dissolved in hydrochloric acid, the solution reduced by sulphurous acid, and the excess of sulphur dioxide boiled off. The arsenic is then precipitated with sulphuretted hydrogen, and the sulphide filtered off. After boiling off the sulphuretted hydrogen, the phosphorus is estimated by the method on p. 358.

Arsenic.—This may be determined by direct methods (see pp. 303 and 360), or it may be estimated from the difference between the figures obtained in the joint estimation of both, and the estimation of phosphorus only by the foregoing methods.

Sulphur.—In soluble ores, and those yielding a white residue of silica only, sulphur may be estimated by the aqua regia method given on p. 349.

In insoluble ores, or in those containing pyrites, and where accuracy is required, fusion with the mixture given above for phosphorus must be resorted to. The melted mass, after boiling out with water, is dissolved in hydrochloric acid, evaporated twice to dryness with the acid to render silica insoluble, and the insoluble residue filtered off. The sulphuric acid in the filtrate is then estimated by barium chloride (see p. 276).

Pure reagents must be employed, and it is desirable to make a blank experiment with the quantities of reagents actually employed. The weight of any barium sulphate thus obtained must of course be deducted from the total obtained in the analysis.

If the ore contains barium, or strontium, or lead, the fused mass must be boiled with water, filtered, and the sulphur in the solution determined by precipitation with barium chloride. The residue is then extracted with hydrochloric acid, and the sulphuric acid in the filtrate estimated separately. The weights of barium sulphate obtained must be added together.

Estimation of Carbonic Acid.—(a) By loss.

Schroder's apparatus (Fig. 84) consists essentially of 3 parts—

1. A light flask, A, of about 75 c.c. capacity, in which the sample of ore is placed for treatment.
2. A bulb, B, provided with a stop-tap and a stopper, in which the hydrochloric acid for decomposing the carbonate is placed.
3. A bulb, C, containing strong sulphuric acid, through which the gas generated must pass in escaping. It is thus dried.

The drying-bulb C is first half filled with strong sulphuric acid, and the bulb B filled with dilute hydrochloric acid. After carefully wiping the apparatus, it should be placed under a desiccator containing sulphuric acid, and after a time weighed with as little handling as possible. From 0.5 to 2 grms. of the ore, in a finely powdered condition,

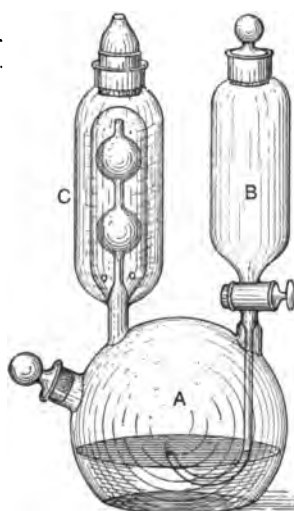
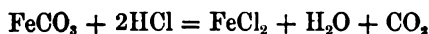


FIG. 84.

is then introduced into the flask, and the whole apparatus reweighed. The tap communicating with the hydrochloric acid is then carefully opened and part of the acid allowed to run slowly down into the flask. The gas generated escapes through the sulphuric acid, and when action ceases, a little more acid is let down. When no more gas is evolved, the apparatus is warmed to expel carbon dioxide, and, after cooling, weighed. The loss of weight is due to expelled carbon dioxide.



The above method answers best for raw carbonates. For estimating the carbon dioxide in oxide ores the best method is as follows: From 5 to 10 grms. of the ore is weighed out into an 8-oz. conical flask, A (Fig. 85), provided with a separator funnel of 100 c.c. capacity, and two leading

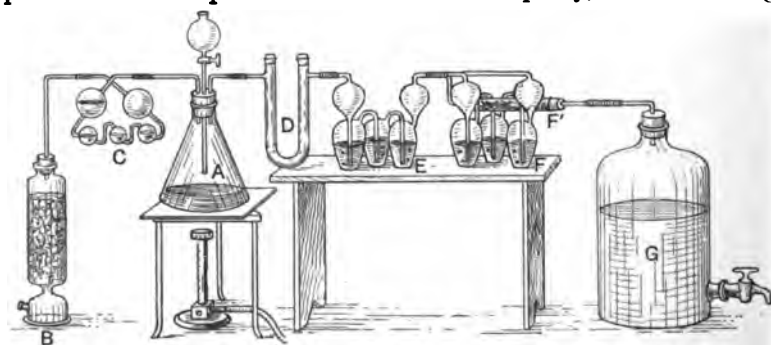


FIG. 85.

tubes. B is a tower filled with fresh soda lime; C is a set of potash bulbs (Liebig's) filled with caustic soda solution; D is an empty calcium chloride tube; E is a set of Geissler bulbs containing strong

sulphuric acid. F is a set of Geissler bulbs filled with strong caustic potash solution (see p. 338); F' is a small calcium chloride tube; G is an aspirator.

The weighed sample is placed in A; the bulbs F are carefully weighed, and the whole apparatus connected. The funnel is filled with dilute hydrochloric acid and the aspirator set going slowly. Some of the acid is then carefully let down. When action ceases the flask is warmed to drive off the carbon dioxide, and the aspirator kept going for some time after the burner is removed. The bulbs F are then detached and reweighed. The increase in weight gives the carbon dioxide. It is better to introduce a second drying-tube between F and the aspirator. This is not weighed, but prevents any possibility of moisture being absorbed from the aspirator.

Alkalies.—When necessary these may be determined as in the analysis of fire clay (see p. 371).

ANALYSIS OF IRON AND STEEL.

THE elements usually requiring determination are carbon—graphitic, combined, and total—silicon, manganese, sulphur, phosphorus, nickel, chromium, aluminium, titanium, tungsten, and molybdenum. Calcium, magnesium, and other metals are seldom present in appreciable quantity.

Estimation of Total Carbon.—The carbon is separated from the iron, and oxidized to carbon dioxide, which is collected and weighed.

The various methods in use for this purpose may be grouped as follows :—

1. Direct burning of the iron borings.
2. Solution of the sample in a copper salt with subsequent oxidation of the carbonaceous residue—
 - (a) by combustion in oxygen ;
 - (b) by treatment with chromic acid.
3. Solution of the sample by electrolytic methods.

Determination of Total Carbon by direct combustion of Iron borings.—The borings require to be absolutely free from oil, grease, etc., and in as fine a state of division as possible. From 1 to 5 grms. are weighed out and placed in a little fire-clay boat,* small enough to go into the tube, made by carefully moistening some fine fire clay and shaping it. The iron is completely covered with magnesia, care being taken that no small particles protrude. The magnesia employed for this purpose must be previously ignited at a high temperature and be quite free from carbonate or other volatile matters.

The boat containing the iron is placed in a porcelain tube containing copper oxide in a short combustion furnace. The ends of the tube protrude beyond the furnace. Calcium chloride tubes and weighed potash bulbs are fitted at one end, and a reservoir of oxygen at the other, with the necessary drying and purification apparatus (see Fig. 88). The tube is heated to bright redness, and then a brisk stream of oxygen is passed through it. The temperature of the tube and the briskness

* These are burnt before use. They are used instead of porcelain, as it is often necessary to break them to see whether the experiment has been successful.

of the oxygen supply are essential features of success. When absorption ceases in the potash bulbs, the oxygen supply is stopped, and the bulbs disconnected and weighed.

When cool the boat is withdrawn from the tube, broken, and examined. If the operation has been successful, the metal will be found to have been completely molten; a red colour, with imperfect fusion, indicates an unsatisfactory result.

This method is less applicable to the estimation of carbon in low carbon steels than in irons richer in carbon. The introduction of copper oxide and copper spirals into the tube, as at p. 338, is not essential, but is an advantage. The method is specially applicable to ferrosilicon, ferrochrome, and other very difficultly soluble bodies. Some analysts recommend the use of powdered fused lead chromate instead of magnesia.

Estimation of Carbon in Iron by Solution of the Metal in a Copper Salt and subsequent combustion.—When iron is brought into contact with a cupric salt the iron dissolves, and copper is precipitated thus—



If the precipitated copper be digested with a cupric salt and hydrochloric acid, the copper is dissolved thus—



The cuprous salt is dissolved in hydrochloric acid or in ammonium and other chlorides. By adopting this method of treatment the carbon in the iron remains undissolved, and may be separated. Its amount is subsequently estimated by combustion.

Solution of Cupric and Ammonium Chlorides (Creath's solution).—172 grms. of pure ammonium chloride, and about 227 of pure crystallized cupric chloride, are dissolved and made up to a litre with water. 50 c.c. of this solution contain very nearly 15 grms. of ammonio-copper chloride, NH_4Cl , CuCl_2 , $2\text{H}_2\text{O}$. 1 gm. of iron requires a minimum of about 8 grms. of this salt to effect its solution.

The solution may be carefully evaporated and crystallized, the crystals washed with water, dried between filter paper, and bottled for use. 15 grms. of the crystals are weighed out for each gramme of iron when required. The ammonium chloride used must be pure and free from tar and organic matters.

The Solution of Copper and Sodium Sulphate and Chloride for the same purpose is made as follows: 350 grms. of copper sulphate is dissolved in about 700 c.c. of water and heated nearly to boiling, and 350 grms. of common salt slowly stirred in. A white precipitate of sodium sulphate falls, which may be rejected. The solution is allowed

to cool, and the liquid is decanted from the crystals of sulphate of soda that separate into a litre flask and diluted to a litre. 50 c.c. of this solution will dissolve 1 grm. of iron.

Solution of the Iron.—Weigh 1 grm. of cast iron or 5 grms. of mild steel in the form of fine drillings, and transfer to a beaker. Add for each grm. of iron 50 c.c. of the copper solution. This is allowed to act on the sample, with frequent stirring at a gentle heat until all the iron is dissolved. This may be ascertained by pressing the precipitated copper with a glass rod to see if any iron remains undissolved. The solution is then heated nearly to boiling (about 90°–95° C.), till the precipitated copper is all dissolved, leaving the carbon, etc., as a residue.

Filtering.—Specially prepared filters free from carbon are neces-

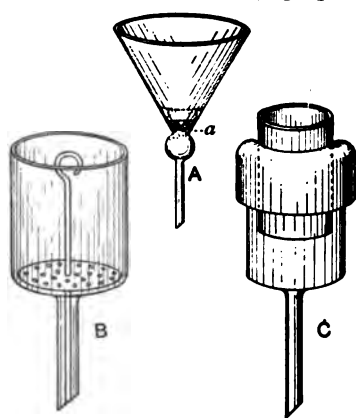


FIG. 86.

sary. They are prepared as follows: Some pure long-fibre asbestos is ignited for about fifteen minutes in a porcelain crucible to remove any organic matter, and cooled, with the lid on to exclude dust. Before ignition it may be moistened with a solution of ammonium nitrate. The ignited asbestos is finely ground with a little water in a mortar, and used to form the filter-bed, which is made as follows: The funnel, A (Fig. 86), is plugged loosely with glass wool at (a), and about half an inch of freshly ignited silica sand placed on the plug. On this is poured sufficient of the

asbestos pulp to form a layer about a quarter of an inch thick, which is allowed to drain dry.

Or a piece of combustion tubing, B (Fig. 86), 1 inch in diameter, is drawn out, as shown, and a finely perforated disc of zinc or copper, with a handle above and below fitted in. A layer of asbestos, coarsely pounded with water, about $\frac{1}{2}$ to $\frac{3}{4}$ inch thick, is first put in, and on this a layer of finely ground asbestos is introduced about $\frac{1}{8}$ to $\frac{1}{4}$ inch thick. The filter thus prepared is placed in the cork of a filtration flask.

Special perforated porcelain crucibles, fitting by means of a rubber cone in a cylindrical funnel, which is placed in the stopper of a filtration flask, are often used to support the asbestos (Fig. 86, C).

The filtration of the solution is accelerated by the employment of a filter pump. F (Fig. 87) is a strong filtration flask having a side

tubulure. The funnel is fitted with a rubber cork. The flask communicates with the air reservoir, R, which serves to steady the vacuum produced by the water-jet pump, P, of which various forms are obtainable. G is a mercury bottle into which a branch of the T connecting tube passes, and fits the neck loosely. The height to which the mercury is drawn in the tube indicates the vacuum obtained. Twenty-seven

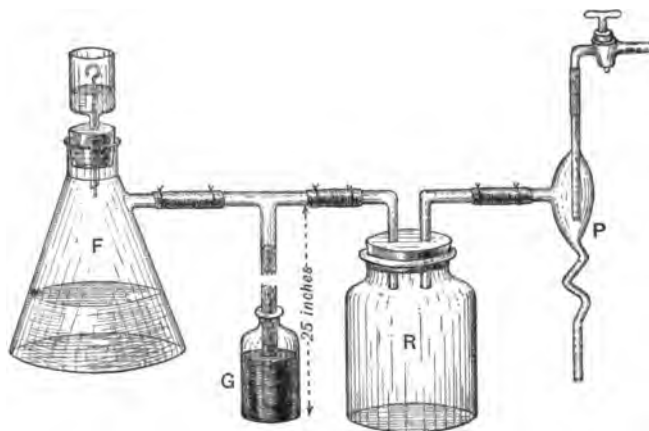


FIG. 87.

inches or upwards is readily obtainable if all connections are tight. Care will be required at first. The vacuum need not be very high if the filter is properly made.

The solution is filtered, and the residue washed with dilute hydrochloric acid (1 acid, 1 water) till free from copper, and afterwards with distilled water. The funnel and its contents are then dried at 100° in the water oven. When dry, the residue is transferred to a platinum boat, and burnt in oxygen (see Fig. 88).

The combustion tube, A, is 28 inches long, half an inch in diameter, and fitted at each end with a perforated cork. The tube must be carefully selected, and before use sponged out and rinsed with distilled water, and carefully dried by a current of warm air. The air may be heated by attaching a piece of brass tube, 6 to 8 inches long, to the bellows-pipe, and heating it in a bunsen, the open end being placed in the end of the combustion tube. The tube is filled as follows: B is a closely wrapped coil of fine copper gauze, 3 inches long. C is a short column of freshly ignited granulated copper oxide, 3 or 4 inches long. D is a similar short column of finer copper oxide. This should pass through a 30-sieve, but all fine dust should be removed by sifting

through a 60-sieve. The columns of copper oxide are kept in place by the asbestos plugs *bca*. These are made of asbestos that has been

moistened with ammonium nitrate, and ignited to ensure absence of organic matter. Short spirals of copper gauze answer even better for plugs. E is the boat containing the separated carbon and asbestos filter. F is a 4-inch coil of copper gauze. These fill about 19 inches of the tube, leaving about $4\frac{1}{2}$ inches at either end unoccupied. G, H, I, K are apparatus for drying and purifying the oxygen. K is a sulphuric acid drying bottle. I is filled with calcium chloride, H with fresh soda lime, and G with caustic soda in small pieces. The other end of the tube is connected with the calcium chloride drying-tube, L, and the potash bulbs, M, which are accurately weighed before being attached.

The potash solution is prepared by dissolving 1 part of caustic potash in 4 of water.

The tube A is placed in an Erlemeyer's or other combustion furnace (Fig. 89), with the ends protruding. A gasholder (Fig. 90), of 2 gallons capacity, containing air or oxygen, is connected at N, by means of which a steady supply of gas may be maintained. If air be used, some form of aspirator may be attached at O and the gasholder dispensed with. In this case a drying tube must be introduced between O and the aspirator. All connections having been made, and the tightness of all joints tested, the heating of the tube is commenced at B, and slowly carried backwards towards E. When the burners under D are lighted, those under F should also be turned up, and, when the tube is well heated, those under E. During the latter part of the preliminary heating an exceedingly slow current of gas is passed through the tube, but when fully heated it may pass more quickly, and so continue till the carbon is completely burnt, and no further absorption in M is seen. This occupies from three-quarters to one hour. When finished, the burners are turned out, and oxygen

or air may be passed through at about the same rate to completely sweep out the carbon dioxide and cool the tube, after which

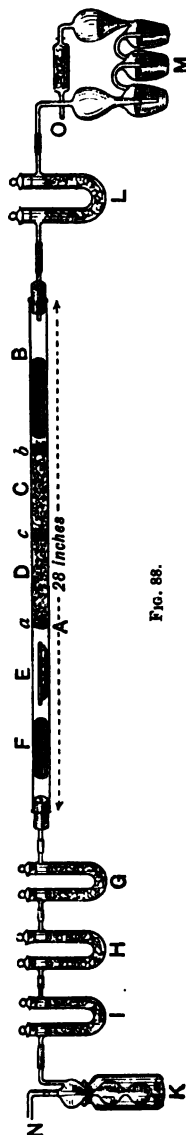


FIG. 88.

the potash bulbs may be detached and weighed. Factor for C, 0.27273.

NOTE.—In weighing potash bulbs the ends should be closed by short pieces of rubber tube, stopped by short bits of glass rod.

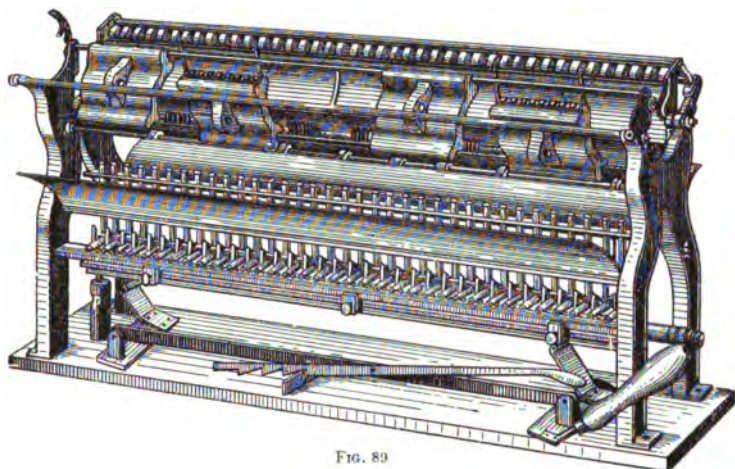


FIG. 89.

The gas current should be regulated so as to pass the potash bulbs at about the rate of one bubble per second. It is occasionally very difficult to burn graphite in dry oxygen, but much easier in moist oxygen. In cases of difficulty a set of Liebig's bulbs containing water may be placed between G (Fig. 88) and the combustion-tube, so as to moisten the gas before entering the tube.

Determination by Oxidation with Chromic Acid.—The separation of the carbon is effected as before, with copper ammonium chloride solution. The residue is oxidized with chromic and sulphuric acids in the apparatus shown in Fig. 91. The carbonaceous residue need not be dried, but may be washed into the flask, A, which has a capacity of 300 c.c., using as little

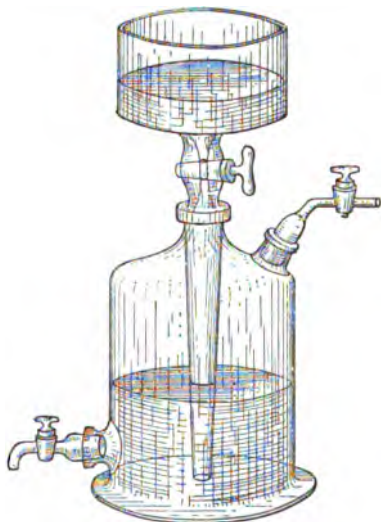


FIG. 90.

water as possible, or may be dried. The 100 c.c. separator funnel, B, contains concentrated sulphuric acid. C is a spiral condenser to prevent steam passing over. D is a tube containing silver sulphate to prevent chlorine or hydrochloric acid passing over. E is a set of bulbs containing strong sulphuric acid. F is a set of potash bulbs. A stream of air from a gasholder, freed from CO₂ by passing through potash, is passed through the apparatus by the tube G. The potash

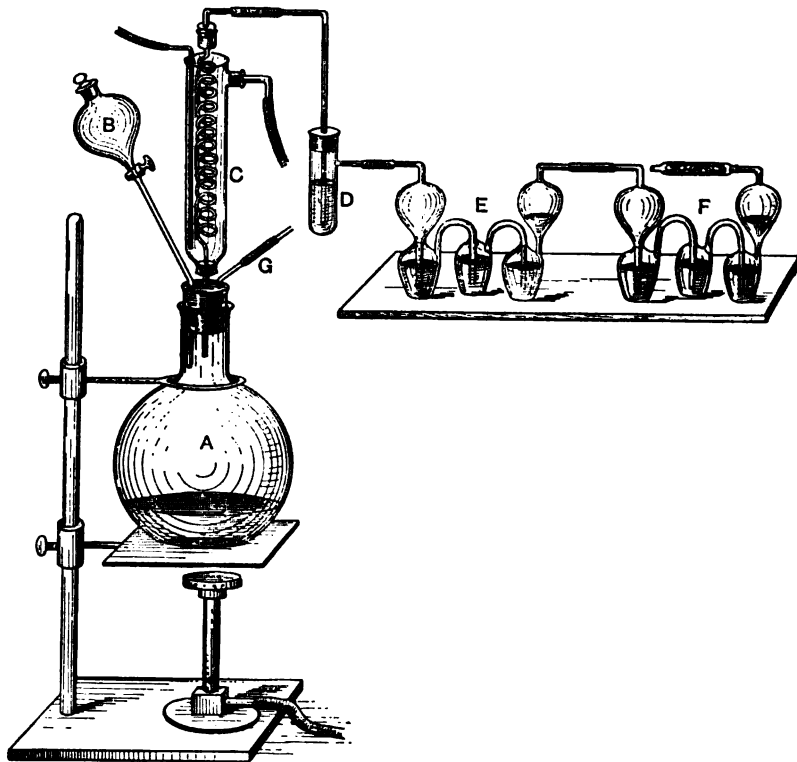


FIG. 91.

bulbs being weighed and attached, the residue is introduced and 10 grms. of chromic acid added. Care must be taken in this, as in all cases, to see that the joints are tight before proceeding with the estimation. Sulphuric acid is gradually added from the funnel from time to time. Gentle heat is applied and the oxidation takes place freely. When the action is complete, and there is no further absorption of carbon dioxide, the potash bulbs are detached and weighed. Increase of weight $\times 0.27273 = \text{Carbon}$.

Weyl's Method.—The Separation of the Carbon by Electrolysis.
—For this process a fragment of iron weighing from 1–5 grms. is placed on a small piece of stout platinum foil, supported from the corners by platinum wires. This is attached to the positive pole of a single Bunsen cell, or a couple of Daniell's cells, and hung in a beaker of dilute hydrochloric acid, near the top. A small strip of copper attached by a wire to the negative—zinc—pole serves as the negative electrode. The negative electrode being placed in the beaker, the tray containing the iron is lowered till it is completely covered by the acid. Solution of the iron commences at once. Hydrogen is given off at the negative electrode and ferrous chloride formed at the positive. Since the hydrogen is set free at the negative electrode, there is no danger of the formation of hydrocarbons and consequent loss of carbon. The solution takes some hours. The residue is not pure carbon, so cannot be weighed directly, but is carefully dried and burnt in oxygen, as on p. 338, and the amount of carbon calculated from the carbon dioxide formed.

Estimation of Graphite.—This may be effected in two ways :—

Method 1.—Two grms. of very grey pig to 10 grms. of spiegel or white, or nearly white, iron, in fine drillings or powder, is weighed and dissolved in 50 c.c. to 100 c.c. dilute hydrochloric acid, preferably in a platinum dish, with the aid of gentle heat in the fume chamber. Further additions of hydrochloric acid may be necessary. The combined carbon passes away in combination with the hydrogen evolved. When the action has completely ceased, the solution is diluted with water and boiled. The residue is allowed to settle, the clear liquor decanted through a filter, allowing as little as possible of the residue to pass on to the filter, and the residue in the basin or beaker well washed with dilute acid. The residue is transferred to a silver dish, using as little water as possible. Any residue on the paper is washed into the dish and the liquid evaporated to small bulk. About 5 grms. of solid caustic soda is then added, and the liquid warmed. A brisk evolution of hydrogen, due to the solution of the silicon, takes place. This occupies about twenty minutes, and when complete the liquid is diluted to 100 c.c., allowed to settle, decanted, and the residue washed by decantation and on the filter till free from alkali. The filter is dried at 120° C., the residue detached and transferred to a shallow weighed platinum crucible, the filter paper completely burnt, and the ash added. The crucible is heated gently with the lid on, and, after cooling in a desiccator, weighed. The crucible is then placed in the muffle and heated to full redness, with free access of air, till the weight is constant. The difference between the final weighing and the first represents the graphite.

If the graphite is difficult to burn, and the residue remains black, the burning may be assisted by moistening the residue with a saturated solution of ammonium nitrate, cautiously drying and igniting it.

Method 2.—The solution of the metal is conducted as in the first method, but the residue is collected on an asbestos filter. After drying, this is burnt in oxygen, and the resulting carbon dioxide collected and weighed as detailed for total carbon (p. 338). If difficulty is encountered in burning the graphite, the oxygen, after purification, should be moistened by bubbling through water (p. 339).

Estimation of Combined Carbon (Eggertz's Colour Test).—When iron containing carbon in the combined form is dissolved in dilute nitric acid under suitable conditions, the solution acquires a brownish tint, the depth of which depends on the amount of carbon, the volume of the solution, and the temperature. By carrying out the solution under proper conditions, the amount of carbon can be determined by a comparison of the tint with that obtained from a sample containing a known percentage of carbon dissolved under like conditions. Or, the comparison may be made with permanent coloured solutions corresponding to known amounts of carbon. The method is simple, and fairly accurate. It is important that the standard sample selected for comparison should contain nearly the same amount of carbon as that to be tested. The percentage of carbon in the standard sample is previously determined by combustion (see p. 336).

Three satisfactory standards are 1.0, 0.4, and 0.2 per cent. or thereabout. The percentage of carbon each contains should be most carefully determined and the metals stored in bars, from which drillings can be taken as required. The samples must be free from rust.

The sample to be tested must be drilled without oil, or crushed in a steel mortar, if too hard to drill. With cast iron the outer skin must be removed prior to drilling. The solution and comparison are conducted in glass test-tubes half-inch diameter. Exactly 0.1 gm. of the standard and 0.1 gm. of the sample, in fine drillings, are weighed out and transferred to the dry test-tubes. If long test-tubes are used, the iron can be introduced by placing it on a narrow slip of stiff smooth paper, sliding it into the tube, and afterwards tilting it. To each of the tubes 2 c.c. of nitric acid, of sp. gr. 1.2, is added. The tubes are marked and placed in a beaker of boiling water till solution is complete, with occasional shaking, and cooled. The "standard" is then poured into a graduated "Eggertz" tube, holding about 20 c.c. and registering $\frac{1}{10}$ ths of a c.c., and diluted with water from a wash-bottle till 1 c.c. = 0.05 per cent.* carbon; *e.g.* if the standard contains

* Many assayers dilute to only half this extent. 1 c.c. = 0.1 per cent. carbon.

0.2 per cent. carbon, dilute to 4 c.c. The sample under examination is poured into a similar tube and carefully diluted with water from a wash-bottle with a fine jet, till the tints in the two tubes are alike. The tube is shaken after each addition, and the liquid let run down completely before finally reading the volume.

The tints are best compared by placing a wetted filter paper behind the tubes, to shade and diffuse the light. When the tints are the same, the volume of the sample is read off, and the amount of carbon calculated, *e.g.* volume of standard = 4 c.c., vol. of sample = 5.8. Then

$$0.2 \times \frac{5.8}{4} = 0.29 \text{ per cent.}$$

Or, if each c.c. = 0.05 carbon, $5.8 \times 0.05 = 0.29$.

In carrying out the test, both the nitric acid employed and the water used must be free from chlorine, the metal free from rust, and the solutions must be cooled prior to comparison. The test-tubes must be of exactly the same diameter. Fresh standards must be made frequently, as the liquor bleaches in a few hours.

In examining cast irons, only 0.05 grm. is taken for the test.

The process is not interfered with by manganese, sulphur, phosphorus—under 5 per cent.—or silicon; but if much silicon be present the solution must settle or be filtered, as the silica renders it cloudy. Copper interferes somewhat by giving a greener tint to the brown colour, but in minute quantities does not vitiate the results. Nickel and chromium also influence the colour, the former giving a greenish, and the latter a greyish tinge. Dilution to 10 c.c., however, destroys the effects on steels containing less than 1 per cent. of these metals. Cobalt gives a reddish tinge, and even 1 per cent. is noticeable till diluted to 50 c.c.

Blodgett Britton employs a larger quantity of the sample—1 grm., and dissolves it in 10 c.c. of nitric acid (1.2 sp. gr.), transfers the solution to a small beaker, and treats the residue in the tube with 5 c.c. more acid. The whole is filtered through a double paper (dry) into a test-tube, $5 \times \frac{5}{8}$, diluted to 25 c.c., and when cold compared with the tubes of a standard set arranged in a rack.

These tubes, which are sealed, contain an alcoholic infusion of roasted coffee, which has been standardized by comparison with a standard steel, and diluted so that No. 1 corresponds to 0.02 per cent. carbon, No. 2 to 0.04, each succeeding one increasing by the same amount up to 0.3 per cent. The comparison tubes occupy alternate holes in the rack. The tube containing the filtered sample is placed in the unoccupied holes, and compared with the tubes on either side, being moved till between those nearest in colour.

For high carbon steels less metal is taken, and for very low carbon steels more, due allowance being made by calculation for the quantity taken. The standard tubes should be kept in a dark place.

Estimation of Silicon.—This element occurs in cast iron to the extent of from 0·5 to 4 or 5 per cent. In silicon irons, and under special circumstances, the amount may be greatly exceeded, and may even reach 16 per cent. In steel, the quantity is, as a rule, small, often not more than a trace, but recent practice favours the introduction of silicon into mild steel for certain purposes, and it is occasionally found in considerable quantity, as much as 0·3 per cent. sometimes being present. This occurs more particularly in steel for wire drawing and in castings. In hard steel silicon is only present in small quantity. Wrought iron frequently includes intermixed slag, which makes the apparent silicon content too high (see p. 346).

In the solution of iron in hydrochloric acid, the silicon remains in the insoluble residue, and is converted into silica by oxidizing agents, in which form it is weighed.

Method 1.—Estimation of Silicon by solution of the Metal in Acid and weighing as Silica.—This method is specially applicable to cast irons containing little or no graphite, and to wrought iron and steel.

From 1 to 2 grms. of cast iron or 2 to 5 or 10 grms. of steel in borings is weighed and dissolved in hydrochloric acid in a 500 or 1000 c.c. beaker. (If it is intended to employ the same solution for the estimation of sulphur and phosphorus, the solution must be effected in a mixture of three parts nitric acid to one of hydrochloric acid (see p. 356), from 20 to 100 c.c. being employed.) When action ceases, about 5 c.c. of strong nitric acid is cautiously added, and the beaker, nearly covered with a clock glass, is put on the hot plate and evaporated carefully to complete dryness. As it approaches dryness, the beaker is moved to a cooler part of the hot plate, to prevent spitting.

When cold, the residue is moistened with hydrochloric acid, and again dried. The beaker is strongly heated—to about 180° C.—for some time to render silica completely insoluble by dehydrating it, and after cooling, the mass in the beaker is moistened with 10 to 50 c.c. strong hydrochloric acid, the clock glass put on, and the liquid warmed, till the iron has gone into solution, and is then boiled. Water is added to about 120 c.c. (it is well to dilute considerably, or filtering will be tedious), and the liquid filtered. Any adhering particles on the side of the beaker are removed with the policeman, and the residue washed with hot dilute hydrochloric acid till free from iron. If the edges of the filter paper retain iron, moisten with strong hydrochloric

acid by means of a dropping-bottle, and wash with weak acid till potassium sulphocyanate gives no coloration, and finally with water till free from acid. The residue on the filter is dried in the air-bath, transferred to a crucible, ignited, and weighed in the usual manner. Time may be saved by drying and igniting the residue in a platinum crucible. The crucible is placed in a muffle, and the graphite remaining with the silica burnt off. When the residue is white, or only faintly yellow, it is weighed. The filter ash is deducted, and the silicon calculated. If the graphite is difficult to burn off, it may be moistened with a little saturated ammonia nitrate solution, dried, and ignited. The precipitate contains 46.729 per cent. silicon.

Method 2.—Sulphuric Acid Method (Drown's Method).—The sample is dissolved in an evaporating basin by cautiously adding, drop by drop, about 10 to 50 c.c. (according to weight of sample) of strong nitric acid, the basin being covered with a clock glass. When all action has ceased, about 3 to 10 c.c. of strong sulphuric acid is added, the liquid kept hot for a quarter of an hour, and afterwards evaporated till fumes of sulphuric acid are evolved. The solution is cooled, diluted to 100–120 c.c., boiled, and filtered hot. The residue on the filter is washed with hot hydrochloric acid, and finally with water. It is afterwards dried, ignited, and weighed.

Method 3.—Estimation of Silicon by treating the residue insoluble in Acid with pure Caustic Soda (Allen's Method).—2 to 5 grms. of the sample is weighed out into a No. 5 evaporating basin, covered with a funnel, or into a 200 c.c. beaker, and dissolved in 30 to 70 c.c. of dilute hydrochloric acid (1:1). The residue is filtered and washed till free from iron. The filtrate contains some soluble silica, and is evaporated to small bulk and reserved. The residue is washed into a silver crucible or dish, using as little water as possible, and if necessary evaporated to about 40 c.c. About 10 grms. of pure potassium hydrate (free from silica) is added to the liquid, warmed for some time, and occasionally stirred. Hydrogen is evolved, and the silicon is oxidized, and, combining with the potash, forms silicate. It is thus separated from the graphite. When the action has ceased, the contents of the dish are washed into a beaker, diluted to 150 c.c., filtered and washed. The filtrate is first acidified with hydrochloric acid, and then added to the filtrate from the insoluble matter. The two solutions are evaporated to complete dryness, and the residue remoistened with hydrochloric acid, dried, and heated to 180° C. Water and hydrochloric acid are added to the residue as before (see Method 2), and boiled till it is dissolved. The silica is filtered off and treated as in Method 1.

The graphite is washed into a small beaker, and evaporated to dryness. The dry residue is treated with 10 to 15 c.c. aqua regia—to dissolve iron, etc.—and boiled. The solution is diluted with water—50 c.c.—filtered, and the residue washed with hydrochloric acid till free from iron; then with water till free from acid. The residue on the filter is either dried or, better, washed down into a platinum crucible with a fine jet of water, and evaporated to dryness in a water-bath, heated to 180° C. in an air-bath, and weighed as graphite.

Afterwards the crucible is heated in a muffle till the graphite is burnt and the residue (SiO_2) deducted from the graphite. It should not exceed from 2 to 5 mgrms.

Estimation of Silicon by Iodine.—This method is suitable for wrought iron, puddled steel, etc.—Where the metal contains slag, the above methods give the total silicon present, whether in the metal or as silicate in intermixed slag. By dissolving the metal in bromine or in iodine, and subsequently dissolving out the silica produced by the action from the residue with pure sodium carbonate, the slag is left unaffected.

From 2 to 5 grms. of the sample in fine drillings or filings is taken, put into a conical flask, with about 20 c.c. water and 10 to 15 grms. of iodine, in a cold place. To secure this, the flask may be placed in a dish containing ice or a mixture of sulphate of soda and hydrochloric acid; it must be covered or provided with a Bunsen valve (see p. 173). Very little gas should be disengaged. The solution occupies some hours, and the flask should be occasionally shaken. When solution is complete, wash down the sides, and dilute with ice-cold, well-boiled water, to prevent the deposition of basic iron salts. The liquid is filtered quickly, disturbing the residue as little as possible. To the residue a few drops of hydrochloric acid are added. If effervescence takes place, the iron has not been completely dissolved. The acid is at once drained off—through the filter—and a little more iodine added, and the flask set aside till the iron is dissolved.

Finally, the residue, consisting of graphite, silica, and slag, is transferred to the filter, and washed till free from iron.

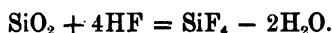
The residue is washed into a silver dish and evaporated to small bulk. 20 c.c. of a saturated solution of pure sodium carbonate is added, and the residue digested on the water-bath with occasional stirring. A metal stirrer should be employed. After an hour's digestion, the liquid is diluted to 100 c.c. and decanted through a tared filter (see p. 52). The residue is again digested, as before, and again decanted. The residue, consisting of graphite and slag, is then thrown on to the filter and well washed with hot water, dried at 120° C., and weighed.

The filtrate is acidified with hydrochloric acid and evaporated to dryness, the residue moistened with hydrochloric acid and again evaporated. The residue is taken up with hydrochloric acid, diluted, boiled, filtered, and washed. The silica is dried, ignited, and weighed as usual. The weighed residue left after treatment with carbonate of soda is ignited in a muffle to remove graphite, and again weighed. The loss is the graphite. It is then treated with a little caustic soda, as in former method, to dissolve silica, and the residue is filtered off, washed, dried, and weighed as slag.

Bromine acts more quickly than iodine, but must be used in a draught chamber.

Testing Silica for purity.—Silica obtained by any of the above methods should be white after ignition. A yellow or darker colour indicates the presence of iron. Phosphoric and titanous irons usually give too high results, owing to the retention of phosphoric and titanous acid in the residue. This error is greater when sulphuric acid is employed than when aqua regia is used, owing probably to the formation of a basic compound, which is insoluble in sulphuric acid, and is white. The error may amount, in some cases, to 20 per cent. of the silicon present. Vanadium, if present, partly remains with the silica.

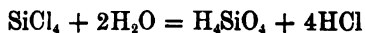
The silica may be treated with excess of pure hydrofluoric acid in a platinum dish, and carefully evaporated to dryness. The loss in weight corresponds with the following equation—



By evaporation the excess of hydrofluoric acid and water are expelled, and the loss of weight is the silica contained in the residue.

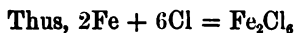
The operation is conducted in a weighed platinum crucible, and a measured quantity of hydrofluoric acid employed. A blank test is made with hydrofluoric acid alone, to determine the amount of solid residue left on evaporation. This is deducted from the weight of residue after hydrofluoric acid treatment, and the result from the original weight of "silica." The difference is the pure silica in the residue.

Method 4.—Estimation of silicon by chlorine.—Suitable for high silicon irons. Iron and silicon, when heated in chlorine, form volatile chlorides. The former is less volatile than the latter, and is deposited in the cooler parts of the apparatus; the silicon chloride when passed into water decomposes thus—



On evaporating the liquid to dryness, the silica is dehydrated, and remains in an insoluble form. Slag included in the metal is not

attacked. The iron is also converted into chloride, which is volatilized and deposited in the tube.



The apparatus is arranged as in Fig. 92.

A, the chlorine apparatus, is charged with permanganate of potash, the separator funnel, B, being filled with strong hydrochloric acid, which is admitted as required.

C is a wash-bottle containing water to remove hydrochloric acid. D and E are sulphuric acid drying-bottles. Other drying apparatus may be substituted. To prevent oxidation and consequent low results,

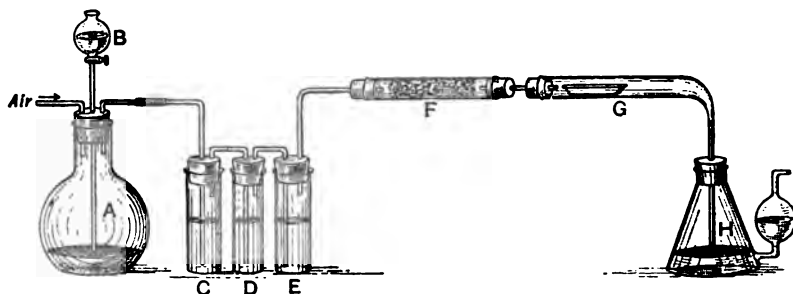


FIG. 92.

the gas is led through a short combustion tube, F, filled with carbon, and heated to convert the oxygen of the air into carbon monoxide. A better plan is to displace the air in the whole apparatus with pure nitrogen from a gas-holder.

G is the combustion-tube, drawn out and bent at 90° so as to just dip into the water in H, which is preferably a nitrogen apparatus. In fitting, the tightness of the corks should be tested.

The sample, about 5 to 10 grms. of wrought iron or steel, is weighed into a porcelain boat. The apparatus being ready and the combustion-tube heated, it is cleared of air and the sample introduced. The temperature is increased to full redness, and a steady stream of dry chlorine passed through the tube, the supply being regulated by the admission of acid from B. Heating is continued till no red vapours are observed near the boat. The after part of the tube will be coated with a reddish-brown deposit of ferric chloride. The silicon tetrachloride formed will be decomposed in H, and hydrated silica thrown down. The contents are emptied into an evaporating basin, and the bulbs washed out with water. The liquid is carefully evaporated to dryness to render the silica insoluble, extracted with hydrochloric acid, and filtered, dried, and the silica ignited and weighed. The determination must be conducted under a hood or in a draught chamber.

The residue in the boat is treated with dilute hydrochloric acid to dissolve iron and manganese remaining in the residue, filtered and dried. It may be weighed—after ignition in a muffle to burn off graphite—as slag, the silica in which may be estimated by fusion with pure sodium and potassium carbonates, as directed (see Analysis of Ganister, p. 379). This, added to that already found, gives the total silicon.

This method is specially suitable for the estimation of silicon in ferro silicon, silico spiegel, and glazed pig iron. It also permits of the discrimination between silicon in the metal and included slag in wrought irons. The residue in the boat may be used for the estimation of carbon.

Estimation of Sulphur.—This element is determined in various ways, The metal is either dissolved in aqua regia and the sulphuric acid formed estimated by precipitation with barium chloride in the solution, or the metal is treated with hydrochloric acid, and the sulphuretted hydrogen and other compounds evolved passed into bromine or other oxidizing agent, to convert them into sulphuric acid. Another method is to collect the sulphuretted hydrogen, etc., in caustic soda and to oxidize with iodine. The latter method yields very varying results.*

Oxidation Method.—Five to 10 grms. of the sample is weighed out and dissolved in 50 to 100 c.c. aqua regia (2 parts hydrochloric acid and 1 part nitric acid), a little pure sodium carbonate added, evaporated to complete dryness in a beaker, and strongly heated on the hot plate. The residue is warmed with strong hydrochloric acid till solution is complete, diluted with water, boiled, filtered, and washed.† The filtrate is nearly neutralized with ammonia heated to boiling, barium chloride added, and boiled for some time. It is set aside for twelve hours, and the precipitate filtered, washed, dried, ignited, and weighed (see p. 280).

Evolution Methods.—Oxidation by Bromine.—The bromine oxidation is conducted as follows. From 5 to 10 grms. of the sample is weighed into a flask of about 500 c.c. capacity, fitted with a safety or separator funnel of 150 c.c. capacity, and delivery tube, which dips to the bottom in the bromine water contained in the flask (Fig. 93). Nitrogen or other bulbs may be used to contain the bromine, constructed so as to expose the gas as perfectly as possible to the action of the bromine. The tube from this dips into a beaker of bromine water to catch any of the solution that may possibly be projected by the violence of the action. The bromine flask is charged with 50–100 c.c. bromine water, 2 grms. of potassium bromide, and 5 c.c. of bromine.

* See Matthewman, *Journal of the West of Scotland Iron and Steel Institute*.

† The filtrate from the silicon determination method may be used.

The weighed sample is placed in the dissolving flask, together with a little pure coarsely ground calcite (2 or 3 grms.), and 100 c.c. of boiled water added. 100 c.c. of strong hydrochloric acid is put into the separator funnel (if used), and it is put in its place. The delivery tube is connected with the absorbing apparatus, the flask being placed on the hot plate, to keep it warm. A little acid is added from the funnel to dissolve the calcite and sweep out the air. Acid is added cautiously, and the flask gently heated to promote solution of the iron. When completely dissolved, the solution is boiled vigorously for a few minutes, to sweep out the last traces of gas, and, while still boiling, the bromine flask is disconnected.

The bromine solution is transferred to a beaker, the bulbs

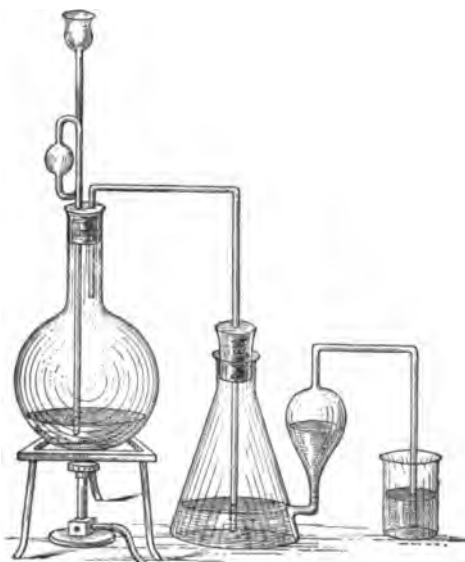


FIG. 93.

washed out, and the solution evaporated till all bromine is driven off. The liquid is treated with hydrochloric acid, boiled, neutralized with ammonia, made up to 150 – 200 c.c., 3 c.c. of hydrochloric acid added, boiled, and while boiling precipitated with barium chloride. The precipitate is dealt with in the ordinary manner (see p. 349).

The solution in the dissolving flask often contains sulphur in various forms, and the whole of the evolved sulphur is not given off as sulphuretted hydrogen. Some of the compounds escape oxidation by

bromine. The method is less reliable than the former, but is in very common use.

The insoluble residue may be examined for sulphur by fusing it with pure sodium and potassium carbonates and a little nitre, boiling with water, and testing the solution, after acidification, with barium chloride.

Absorption in Caustic Soda.—The collection of the gaseous sulphur compounds in caustic soda is sometimes resorted to, in which case about 20 c.c. of caustic soda solution, 1 part in 4 of water, is placed in the apparatus (Fig. 94), which is attached to the dissolving flask. In this case the calcite must be omitted and the air displaced by hydrogen, unless a very large excess of caustic soda is used. When the action has ceased, the bulbs are rinsed out into a beaker, the solution diluted somewhat with bromine water, and 2 c.c. of bromine carefully added. The liquid is then cautiously acidified with hydrochloric acid, the solution heated, and the sulphate precipitated with barium chloride, and dealt with as before.

Morrell's Method.—The gases evolved are passed through an ammoniacal solution of cadmium sulphate, and the precipitated cadmium sulphide collected on a tared filter, washed, dried at 100°, and weighed.

Colorimetric Methods, depending on the depth of tint produced by the action of the evolved gas, on metallic silver and salts of metals, are, at best, only rough indications, but may be used for rapid work, and in testing the freedom of the metal from injurious quantities of sulphur.

Eggertz's Test for sulphur is conducted as follows:—0.1 gm. of the iron in fine drillings is introduced into a flask or bottle, 6 inches high and 2 inches in diameter, containing 1.5 c.c. of sulphuric acid, sp. gr. 1.25 (2 parts water, 1 concentrated sulphuric acid). A strip of foil, $\frac{3}{4} \times \frac{3}{4}$ inch, composed of 75 per cent. silver and 25 per cent. copper, hung by a wire of silver or platinum, is quickly introduced into the flask, and a loosely fitting cork put on. It is allowed to stand 15 minutes. The silver plate on removal is compared for colour with standards, varying from coppery yellow, bronze brown, bluish brown, to blue. Steel, sufficiently free from sulphur, does not give more than a yellow, inclining to brown. Pig iron seldom gives less than blue-brown to blue. The strips

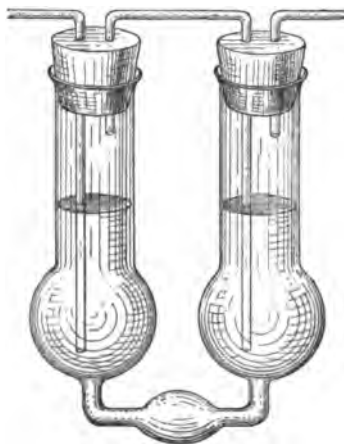
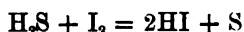


FIG. 94.

of foil should be washed in alcohol and ether, and placed in position for comparison without handling.*

Estimation of Sulphur in Iron and Steel by means of Iodine.—Elliot's Method.—This method depends on the evolution of sulphuretted hydrogen when the iron is dissolved in hydrochloric acid, and the conversion of iodine in solution into hydriodic acid by the gas.



Hence, by taking a known quantity of iodine, and estimating the excess after the passage of the gas evolved by treatment of the steel with hydrochloric acid through it, by standard thiosulphate of soda, the amount of sulphur can be determined.

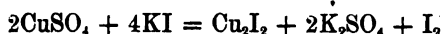
In practice it is usual to first absorb the H_2S in caustic soda, as described on p. 351.

Standard Iodine Solution.—Dissolve 6.5 grms. of pure iodine in water by means of 9 grms. of potassium iodide, and make up to 1 litre.

Standard Thiosulphate of Soda.—Dissolve 25 grms. of the salt in water and make up to a litre.

Starch Solution.—Grind 0.5 gm. of starch (arrowroot starch is best) in a mortar and add water to a thin cream. Pour gradually into 250–300 c.c. of boiling water, boil up and let stand till cold. Use the clear solution.

Standardize the Thiosulphate Solution with pure electrotype copper, as given on p. 86, but express results in iodine, thus—



Hence 127 parts of copper liberate 254 of iodine, *i.e.* 1 part of copper is equivalent to 2 of iodine, and a simple multiplication of the copper standard by 2 gives the iodine equivalent. At least two experiments should be made, and the results should agree.

Standardizing the Iodine.—Measure 25 c.c. of the thiosulphate solution into a beaker, add a little starch, and titrate with the iodine solution till the blue colour appears. The strength of the iodine solution is calculated from the known strength of the thiosulphate.

The Analysis.—From 1 to 10 grms. of the steel is dissolved in hydrochloric acid, and the evolved gas passed through caustic soda as in the method given above. Sufficient sulphuric acid to neutralize the caustic soda in the bulbs is put into a beaker, and a measured quantity of iodine solution, say about 20 c.c., is added, and the caustic soda

* See *Crooks' Select Methods of Chemical Analysis*, 2nd edit.

solution from the bulbs cautiously added. The excess of sulphuric acid is then exactly neutralized with caustic soda, the final neutralization being made with a 1 per cent. solution. The remaining free iodine is then estimated by the addition of 10 c.c. starch paste and careful titration with the standard sodium thiosulphate. Care must be taken that the volume is kept as small as possible. The difference between the weights of iodine added and found multiplied by 0.12637 gives the weight of sulphur in the sample.

Estimation of Manganese.—This metal is usually estimated either by precipitation as hydrated dioxide by means of bromine, and weighing as Mn_2O_3 , or by means of a standard solution of potassium permanganate. Traces are estimated colorimetrically by converting it into permanganate by boiling with lead peroxide and nitric acid, and estimating the quantity by the depth of colour produced. It is also occasionally determined as phosphate.

Bromine Method.—This method is most commonly used. It is conducted by dissolving from 0.5 grm. of ferromanganese to 2 grms. pig iron, or 10 grms. of steel in hydrochloric acid, with the aid of heat in a covered beaker. Nitric acid is added to peroxidize the iron, and the solution evaporated to dryness, and strongly heated on the hot plate. The residue is taken up with a little hydrochloric acid and warmed till solution is complete. The solution is then diluted to about 120 c.c., and if there be much residue it may be filtered. This, however, is not essential. The solution is transferred to a beaker capable of holding a litre, and is diluted to at least half a litre with boiling water, and is then partially neutralized with ammonium carbonate, and finally with dilute ammonia. The success, as well as the rapidity, of the process, depends on how carefully this is done. It is impossible to neutralize a solution of ferric chloride quickly without producing a precipitate. Reference to the chemical properties of manganese will, however, show that it is not readily precipitated by ammonia in solutions containing ammonium salts, and that precipitation in acid solutions is almost impossible. In neutralizing, the addition of the ammonia is, therefore, continued till the liquid contains a precipitate of ferric hydrate, but is still distinctly acid to litmus. Near the end the solution is heated to about 80° C. and dilute ammonia is employed, with constant stirring. It is then heated nearly to boiling, and from 10–40 grms. of ammonium or sodium acetate in solution added to the liquor. The addition of a sufficient excess of the acetate to completely remove the iron is an important factor in the success of the operation. The liquor is then boiled for a few minutes, when the iron separates as basic acetate of a brick-red colour.

The liquor is quickly filtered through a large filter of cellular paper, using a ribbed funnel, and the precipitate thoroughly washed with boiling water.

NOTE.—This filtration and washing is often tedious. In many works the solution after precipitation is cooled, made up to a litre in a measuring flask, well shaken, and half a litre filtered through a dry paper into a 500 c.c. flask. The manganese is determined in this quantity, so that the original weight of the sample must be divided by two. The space occupied by the precipitate is not great, but when 10 grms. is taken the dilution before filtration should be greater than a litre.

The filtrate should be colourless, bright, and clear. Any yellow tinge indicates the presence of iron and the necessity for reprecipitation or filtration. If the presence of iron be suspected, the filtrate should be tested by evaporating to small bulk with a further addition of ammonium acetate. If the precipitation be complete, the filtrate is cooled, and bromine water and 5–10 c.c. of bromine is added. The solution is made strongly alkaline with ammonia, and boiled for some time. It must remain distinctly alkaline to the end. The precipitate of hydrated peroxide is allowed to settle, filtered, washed thoroughly, dried, ignited strongly (preferably in muffle), and weighed. The manganese filtrate should be evaporated to small bulk, and tested with bromine water and ammonia, any precipitate produced being added to that first obtained. Copper, if present, is thrown down with the manganese, and must be removed by sulphuretted hydrogen before precipitating the iron.

With spiegeleisen and manganiferous pig iron the iron precipitate often carries down a little of the manganese. Its presence may be detected by the lead peroxide test given on p. 199. If manganese be present, it is necessary to filter all the solution, dissolve the precipitate from the filter, without washing, in hydrochloric acid, and reprecipitate with ammonia. The two filtrates obtained must then be evaporated to smaller bulk, and treated as before.

For the estimation by permanganate, see pp. 206–207, Manganese.

Colorimetric Estimation (*see* Manganese, p. 208): 0.1 gm. of the steel is dissolved by boiling with 3 to 4 c.c. of nitric acid (sp. gr. 1.2) in a test-tube; 0.2–0.5 gm. of lead peroxide is added and again boiled. The solution is cooled, filtered through ignited asbestos (no organic matter must be present) into an Eggertz tube (*see* Carbon), having a capacity 50 c.c., and the filter washed thoroughly. The colour is compared with that produced by a standard solution of permanganate, or a similar quantity of steel, the manganese content of which is known as in making carbon tests (*see* p. 342). For substances containing over 0.5 per cent. of manganese the solution is divided so as to obtain a solution containing not more than 0.0005 gm.

The standard is made by dissolving 0.316 gm. of potassium permanganate in 100 c.c. water and diluting 5 c.c. of this solution to 550 c.c., each c.c. = 0.00001 gm. Mn.

A better method of colour comparison is to use two Nessler tubes—one of which has a tap at the bottom—standing on a white tile. The solution under examination is diluted to 50 c.c. in one, and nearly 50 c.c. of water is placed in the other tube standing alongside. Over this is a burette charged with a solution of permanganate, which is run in, mixed with the water, and the colour compared by looking down through the liquid. Additions of the permanganate are made till the depth of colour is the same. If the added solution raises it above the mark it is run off by the tap at the side till the heights are identical. When the tints are equal, any excess of liquid is measured and the permanganate it contains deducted from that used from the burette. In following this method a larger sample must be taken than in the method given above.

A solution of potassium permanganate may be made; 0.316 gm. dissolved in 1 litre, each c.c. = 0.00011 gm. of manganese.

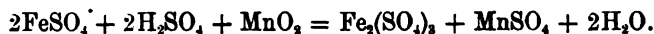
Estimation of Manganese in Chrome Steels and Ferro Chrome.—The chromium is removed as chromate in the case of ferro chrome by fusion, and in chrome steels by treatment with nitric acid and potassium chlorate (Ford and Willans's method).

For ferro chrome, 1 to 2 grms. is taken, and fused with an oxidizing mixture (see pp. 364, 365). The mass, after fusion, is extracted and treated as there directed, the residue containing the iron and manganese being filtered off and slightly washed. It is then washed down, and dissolved by hot strong hydrochloric acid in the beaker in which the extraction took place. The solution is evaporated to small bulk, diluted largely, the iron removed by acetate, and the manganese precipitated with bromine in the usual manner (see p. 353).

For chrome steels, 5 grms. of the metal is dissolved in strong nitric acid, potassium chlorate added, and evaporated nearly to dryness. This is repeated three times. The liquid is then diluted, rapidly filtered, and the residue thoroughly washed. The residue is transferred to a flask containing a known weight of acid ferrous sulphate (see p. 201), and warmed till solution is complete. The excess of ferrous sulphate is then determined by potassium bichromate. The amount of iron oxidized by the manganese peroxide in the residue is obtained by deducting that found by the bichromate estimation from the weight added. This, multiplied by 0.491, gives the manganese present.

When the steel is dissolved, the manganese is left as hydrated

peroxide. This, as it dissolves in acid ferrous sulphate, peroxidizes a portion of the iron present; thus—



Estimation of Phosphorus.—Two methods are in common use for the estimation of this element—

- (1) The phosphorus is oxidized to phosphoric acid, and the phosphoric acid precipitated by ammonium molybdate;
- (2) Precipitation of the phosphoric acid by magnesia mixture.

A volumetric method by means of uranium acetate is also employed.

Precipitation by Ammonium Molybdate.—The addition of ammonium molybdate to a solution containing phosphoric acid, acidified with nitric acid, precipitates, on warming, a heavy golden-yellow precipitate, consisting of phosphomolybdate of ammonia, having a composition $(\text{NH}_4)_3\text{11MoO}_3\text{PO}_4\cdot 6\text{H}_2\text{O}$, insoluble in dilute nitric acid, and containing only 1.63 per cent. of phosphorus. This precipitate may be dried at 100°C . without alteration.

The ammonium molybdate solution may be prepared by dissolving 40 grms. of powdered ammonium molybdate in hot water, and diluting to 500 c.c., and filtering if necessary.

From 0.5 grm. of pig iron to 5 grms. of steel in fine drillings is placed in a half-litre beaker (20 ozs.), covered with a clock glass, and dissolved in 30 to 50 c.c. of a mixture of 3 parts nitric acid and 1 part strong hydrochloric acid, and heated till solution is complete. It is diluted to 50 c.c., and filtered if necessary. In iron and steel containing much silicon, the weight of silica subsequently found may be deducted from the precipitate obtained. Any other insoluble matters, such as graphite, scale, tungsten, etc., must be filtered off before proceeding, washed, and the solution evaporated to 50 c.c.

NOTES.—In steels and irons containing more than 1 per cent. of combined carbon, it is necessary to evaporate to dryness, and heat strongly to destroy carbonaceous matter.

The iron must be in *nitric* acid solution. The presence of chlorides is objectionable, hence the omission, where possible, of evaporating with hydrochloric acid to render silica completely insoluble. If evaporation is necessary it is conducted in the beaker on the hot plate, and the residue heated till no red fumes come off. After cooling, it is dissolved in strong hydrochloric acid on the hot plate, twice the volume of nitric acid added, and evaporated to small bulk to remove hydrochloric acid. Many analysts follow this course in all cases.

The solution is then allowed to cool, the beaker rinsed down with warm water, and a slight excess of ammonia added to completely precipitate the iron as ferric hydrate.

The precipitate is then carefully dissolved in hot nitric acid, *sp. gr.*

1.21 (1 part HNO_3 , 1 part H_2O), adding the acid in small portions at a time to the beaker standing on the hot plate, till solution is complete; 3 c.c. of strong or 6 c.c. dilute nitric acid is then added in excess. The total volume should not exceed 90 c.c. Some chemists recommend a maximum volume of 50 c.c. The beaker is removed and let cool somewhat, and 15–20 c.c. of the molybdate solution carefully added, with gentle shaking. The free nitric acid and ammonium salts present should prevent the precipitation of white molybdic acid, and a golden-yellow precipitate *only* should form. The solution is heated to 80° – 90° C. on the hot plate for some time, or heated just to boiling-point, stood aside for 15–20 minutes, till the precipitate formed settles readily, and filtered through a 9 c.m. tared filter paper, prepared as described (p. 52). The precipitate is washed by decantation with 2 per cent. nitric acid, and finally transferred to the filter by a jet of the acid, and washed with acid on the filter till free from iron and the filtrate is no longer yellow.

The precipitate is dried at 100° and weighed, the papers being separated, one going to the side on which the weights are placed.

If a specially smooth filter paper be used, the precipitate may be detached from the paper, and weighed on a watch-glass. A loss of one or two milligrammes occurs, but this scarcely influences the result, as the precipitate contains so little phosphorus.

Professor Arnold recommends washing the precipitate from the paper into a weighed porcelain dish, and evaporating to dryness on a water-bath, finally heating to 100° , and weighing.

The precipitate should be kept in a desiccator, or weighed as soon as dry, as it is slightly hygroscopic. The weight multiplied by 0.0163 = the weight of phosphorus in the precipitate.

This process requires for success the presence in the solution of a limited amount of free nitric acid, a large proportion of ammonium salts, preferably nitrate, and the addition of a considerable excess of molybdate. The nitric acid and ammonium salts are necessary to prevent the precipitation of molybdic acid, and basic compounds of iron and the excess of molybdate to ensure complete precipitation.

Prolonged digestion or boiling yields high results by precipitating molybdic acid. It is, however, easy to prevent its precipitation, but should it be thrown down, the whole of the precipitate must be dissolved in ammonia and reprecipitated by addition of nitric acid.

The presence of the phosphorus as orthophosphate is essential, as pyro and meta phosphates are not precipitated.

Riley and Blair recommend the use of a nitro molybdate solution instead of simple molybdate. This is prepared by dissolving 25 grms.

molybdic acid in 100 c.c. of dilute ammonia (2 ammonia, 3 water). This solution is poured into 400 c.c. of nitric acid (sp. gr. 1.2), with constant stirring, warmed to 70°–80° for a short time, set aside for a day, and filtered. It should give no precipitate on boiling. On long standing, a yellow precipitate of undetermined composition separates.

Magnesia Process (Riley's Method).—In this process the phosphorus is oxidized with nitric acid, and the phosphoric acid produced precipitated by magnesia mixture as ammonio-magnesium phosphate, $\text{NH}_4\text{MgPO}_4\cdot 6\text{H}_2\text{O}$, which on ignition loses ammonia and water, yielding $\text{Mg}_2\text{P}_2\text{O}_7$, pyrophosphate of magnesium.

Magnesia Mixture.—The magnesia mixture is made by dissolving 50 grms. of magnesium chloride and 50 of ammonium chloride in 300 c.c. water, and adding 150 c.c. of strong ammonia solution. The solution should be allowed to stand 3 or 4 days, and then filtered into a bottle for use.

The iron is obtained in solution as before, using an excess of nitric acid; but the presence of chlorides does not affect the operation, so that evaporation to dryness with hydrochloric acid and strong heat may be resorted to to completely separate silica, etc. The residue is dissolved in strong hydrochloric acid on the hot plate (see p. 344), diluted, filtered, and the paper washed, using a dropping-bottle to moisten the edges of the paper with acid. The solution is partially neutralized with ammonia, and the iron reduced to the ferrous condition with sulphurous acid or sodium sulphite. Any excess of the latter must be decomposed by hydrochloric acid. Excess of sulphurous acid is expelled by boiling, and a few drops of bromine water added. Ammonia or sodium carbonate is then added till neutral, then about 10 grms. of sodium acetate, and the solution boiled. The precipitate contains the whole of the phosphoric acid. It is filtered quickly while hot, the filtrate rejected, and the precipitate dissolved without washing in about 25 c.c. dilute hydrochloric acid (1 : 1), warmed in the vessel in which the precipitation took place, to dissolve any adhering precipitate. Both vessel and filter are thoroughly washed with acid and water, and the solution evaporated to about 50 c.c. About 5 grms. of citric acid is added to prevent the precipitation of the iron, a few c.c.s. of magnesia mixture added, and then ammonia till strongly alkaline. After standing 24 hours, till precipitation is complete, the liquid is filtered, care being taken to remove the precipitate from the sides of the beaker. If the precipitate does not come off by rubbing with a rubber-tipped glass rod (policeman), a drop or two of hydrochloric acid must be used to dissolve it, and the solution reprecipitated by adding excess of ammonia. The filtrate

must be measured, and the dissolved precipitate allowed for (see below). The precipitate is washed with dilute ammonia (1 in 3), dried, ignited (gently at first and afterwards in a muffle), and weighed. It should be quite white. Factor for P = 0.27953.

The precipitate is slightly soluble in the solution to the extent of 0.001 grm. per 30 c.c. The volume of the filtrate should be measured and the correction made.

Arnold's Combined Method by means of Molybdate and Magnesia mixture.—The precipitation of the phosphoric acid by molybdate is carried out as above, but the solution may be heated to boiling, as any molybdic acid precipitated is subsequently got rid of. The yellow precipitate is collected on an ordinary filter and washed free from iron with dilute nitric acid as before. The funnel is placed over a small beaker, the precipitate dissolved in the smallest possible quantity of hot dilute ammonia, and the paper well washed with hot water. Any molybdic acid that may have been precipitated is dissolved in the excess of ammonia, and 2 c.c. of strong hydrochloric acid is added to form ammonium chloride, or that salt may be added in solution. The liquid is made up to about 50 c.c., and 2 or 3 c.c. of magnesia mixture added. The solution is vigorously stirred and let stand 24 hours, after which the precipitate is filtered, washed, dried, ignited, and weighed as before. Allowance must be made for the solubility of the precipitate.

In Spiegeleisen and Ferromanganese, Siliconeisen and Tungsten Iron, 10 grms. of the sample is treated in nitric acid, sp. gr. 1.21, till solution is complete—a tedious operation. The solution is evaporated to dryness, and heated on a hot plate for 1 hour. The residue is taken up with strong hydrochloric acid and all chlorine boiled off. 10 grms. of ferrous sulphate is then added, the liquid evaporated to very small bulk with addition of hydrochloric acid (to eliminate As, which see), water added, and the solution filtered. The filtrate is nearly neutralized, and sodium sulphite added to reduce the iron. Excess of sulphur dioxide is removed by boiling, a drop or two of bromine water added to peroxidize a little of the iron, and some acetate of ammonia. The liquid is then heated to boiling and the precipitate of basic acetate—containing all the phosphorus—filtered off. The filtrate is removed, and a small beaker substituted. A little hydrochloric acid—heated in the flask in which the acetate precipitation took place—is then poured over the precipitate to dissolve it, and the paper well washed. The solution is evaporated,* if necessary, citric acid added, and the phosphorus determined by the magnesia method.

* Arsenic, unless previously separated, may also be removed at this point by adding a few drops of sodium sulphite solution and evaporating to very small bulk.

Estimation of Arsenic.—In the estimation of phosphorus by the foregoing methods, the arsenic present is also thrown down, since in dissolving the iron the arsenic is converted into arsenic acid, which behaves like phosphoric. Hence, in the last method given, the arsenic acid was reduced by ferrous sulphate to arsenious acid, and on evaporation with hydrochloric acid, expelled as the volatile arsenious chloride. Arsenic is thus eliminated.

In estimating it, advantage is taken of the precipitation of its yellow sulphide by sulphuretted hydrogen in acid solution. After separation, it is converted into arsenic acid, and estimated by precipitation with magnesia mixture.

It is also estimated by distillation with ferrous sulphate.

Sulphide Process.—10 grms. of the metal is dissolved as for phosphorus estimation, evaporated, heated, and taken up with 40 c.c. strong hydrochloric acid at a low temperature. The solution is diluted to 250–300 c.c. in a large flask, nearly neutralized, and the iron, etc., reduced by sodium sulphite or sulphurous acid. The excess of sulphur dioxide is boiled off, and the warm liquor saturated with sulphuretted hydrogen. The flask is corked and set aside for 4 to 5 hours.

The liquor is filtered through an 11 c.m. paper, and the precipitate thoroughly washed with dilute hydrochloric acid (1 : 10, or a little stronger) till free from iron. It consists of As_2S_3 and possibly other sulphides, in which case it may be dark coloured.

The precipitate is washed off the filter into a conical flask with a little warm dilute ammonia, and the flask in which the precipitation took place is also washed out with ammonia and added to the rest of the solution. Strong nitric acid is cautiously added in excess, the flask being inclined sideways to prevent loss by spitting, and the liquid boiled down to very small bulk till the sulphur has dissolved.

The solution is then made strongly alkaline with ammonia. No precipitate of ferric hydrate should form. If it does, it must be dissolved by hydrochloric acid, and the reduction and precipitation with sulphuretted hydrogen repeated. 2 or 3 c.c. magnesia mixture is added to the ammoniacal solution, which is treated as for estimation of arsenic on p. 250, the precipitate being dried at 100° on a tared paper till the weight is constant. It contains 39.49 per cent. of arsenic. An addition of 1 mgrm. per 16 c.c. of the original filtrate must be made, to allow for the solubility of the precipitate.

Estimation by Distillation with Ferrous Sulphate.—Ten grms. of metal is dissolved as before, evaporated to dryness, heated, and carefully taken up with hydrochloric acid. The solution is transferred to a retort attached to a condenser, a large quantity of ferrous sulphate

added, and the liquid distilled till the residue is nearly dry. The distillate, which should be quite colourless, is nearly neutralized with sodium carbonate, cooled, sodium bicarbonate added in excess, and dealt with as on p. 303.

Arsenic is seldom present in sufficient quantity to yield good results by this method.

ANALYSIS OF FERRO ALUMINIUM.

Aluminium.—0.5 grm. of the alloy in a fine state of division is dissolved in strong hydrochloric acid and evaporated to dryness. The residue is heated with hydrochloric acid, the insoluble matter filtered off, well washed with hydrochloric acid, nearly neutralized with ammonia, and sulphurous acid added till the iron is reduced to the ferrous state (not to be precipitated by sodium acetate), and excess of sulphur dioxide is expelled by boiling. A little sodium phosphate is then added, and the solution slightly acidified with acetic acid. The liquid is heated to boiling, 30 c.c. ammonium acetate solution added, and the boiling continued for 5 minutes. The precipitate is allowed to settle, filtered, and washed by decantation. The precipitate is dissolved by pouring boiling hydrochloric acid over the filter, the solution being received in the beaker in which the precipitation took place, and the filter is washed. The solution is then transferred to a silver dish, evaporated nearly to dryness, and an excess of pure caustic soda, NaHO , added (about 5 grms. of soda is required = 3 grms. of sodium). The solution must be kept as concentrated as possible. It should not exceed 40 c.c.

The caustic soda is made from metallic sodium in a silver dish. Unless made as required, the solution must be kept in a gutta-percha or metal bottle, as the silica, etc., dissolved from glass or porcelain, would be thrown down subsequently with the alumina.

The soda is well stirred in, and the liquid kept at boiling point for about 10 minutes. After cooling, it is diluted to about 50 or 80 c.c., and the precipitated ferric hydrate filtered off and washed. The filtrate containing the aluminate and phosphate of soda, etc., is then acidified with hydrochloric acid, pure sodium phosphate added in excess, the solution made alkaline with ammonia, and kept at boiling point till the precipitate collects. After settling, the liquid is decanted through a filter, the precipitate washed by decantation, and, finally, on the filter, till free from chlorine, dried, ignited, and weighed as AlPO_4 . It contains 22.36 per cent. of aluminium.

In estimating aluminium in steel or iron, it is necessary to redissolve

the first precipitate obtained with ammonium acetate, and reprecipitate after reduction with sulphur dioxide in order to free it from iron.

Stead's Process.—11 grms. of the metal is dissolved in a 20-oz. beaker in 50 c.c. strong hydrochloric acid, and evaporated to dryness. The residue is warmed with 5 c.c. strong HCl, 50 c.c. of boiling water added, the solution filtered, and the residue washed free from iron. To the filtrate a little sodium phosphate is added, and the solution neutralized with ammonia, till a permanent precipitate is produced. This is just dissolved by HCl, added drop by drop, the solution heated to boiling, 50 c.c. of a saturated solution of sodium thiosulphate added, and the liquid boiled for an hour. The precipitate is filtered and washed, dissolved in 10 c.c. dilute hydrochloric acid (1 : 1), the filtrate being received in a platinum dish, and the filter washed. The solution is evaporated, 5 grms. of pure caustic soda in strong solution added (see above), evaporated to dryness, and fused for 10 minutes. The melted mass, after cooling, is boiled out with 50 c.c. water, and made up to 110 c.c. The residue is filtered off, 100 c.c. of the filtrate taken (= 10 grms. iron), neutralized with strong hydrochloric acid, 30 c.c. of a saturated solution of sodium thiosulphate, 3 c.c. of a 10 per cent. solution of sodium phosphate, and a little sodium acetate solution are added, the solution boiled for a few minutes, and the precipitate is filtered, washed, dried, ignited, and weighed as AlPO_4 , containing 22.36 per cent. of aluminium. The process depends on the precipitation of the aluminium as phosphate, while the precipitation of the iron is prevented by its reduction to the ferrous state by the thiosulphate added. The fusion and reprecipitation ensure the complete removal of any iron or manganese carried down by the first precipitation.

With Tungsten steels the tungsten can be removed by evaporating the original solution to dryness with nitric acid and filtering. The reduction with sulphur dioxide is, however, more difficult.

ANALYSIS OF IRON AND STEEL CONTAINING CHROMIUM, NICKEL, TUNGSTEN, VANADIUM, AND MOLYBDENUM.

CARBON, silicon, manganese, sulphur, and phosphorus are determined by methods already given.

Estimation of Chromium.—The determination of this constituent is made by converting the metal into chromate and estimating it in that condition. Alloys containing much chromium are treated at once for conversion of the metal into chromate by fusion with oxidizing agents. Poorer alloys are first dissolved in acid, and the residue, after evaporation, oxidized by fusion with oxidizing agents, or as on p. 213.

Gravimetric Determination of Chromium in Steels (Arnold).—Two grms. of the steel in fine drillings is dissolved in 40 c.c. hydrochloric acid (1 : 1) on the hot plate, and the solution carefully evaporated to dryness in the beaker. The crisp residue is removed from the beaker on to a clock glass, or evaporating basin. Any remaining in the beaker is dissolved in the minimum amount of hydrochloric acid, the liquid poured into a platinum basin, evaporated to dryness, and the dry mass previously removed added and crushed with a flattened glass rod. 5–7 grms. of a mixture of 2 parts potassium nitrate, 1 part potassium carbonate, 1 part sodium carbonate, is then added in successive portions and well mixed by the glass rod, which may be cleaned with a little of the mixture, which is afterwards added to the melt. The whole is then fused in a muffle, or over a good bunsen for 15–20 minutes, and allowed to cool. The iron is thus converted into Fe_2O_3 , and the silicon, chromium, manganese, and sulphur into silicate, chromate, manganate, and sulphate respectively. The melted mass is boiled out with 100 c.c. water in a beaker, and the basin washed. The solution will probably be green, due to the presence of manganate, to reduce which 3 or 4 drops of alcohol is added, and the liquor warmed. The manganese after reduction is precipitated as carbonate in the alkaline liquid (p. 200). After settling, the clear solution is carefully decanted through a double

paper, care being taken not to disturb the precipitate. The residue is washed by decantation thus:—30 c.c. boiling water is added, and, after settling, filtered. The filter paper is then washed twice with water. Another 30 c.c. of water added to the residue in the beaker, and the paper again washed. This is considered sufficient. The solution now contains the silicate and chromate. To separate silica, hydrochloric acid is carefully added to the alkaline liquor in excess, boiled till carbon dioxide is expelled, and evaporated to small bulk. The solution (green chromic chloride) is made alkaline with ammonia, heated to boiling, and the precipitate of hydrated chromic oxide and silica filtered off. It is dissolved in hot dilute hydrochloric acid, the paper washed, the solution being received in the beaker in which precipitation took place, and evaporated to dryness. The residue is taken up in 100 c.c. dilute hydrochloric acid (1 in 9), the silica filtered off, and the solution made slightly alkaline with ammonia and heated nearly to boiling point. After settling, the precipitate is filtered off, dried, ignited, and weighed as Cr_2O_3 , containing 68.64 per cent. of chromium. This method is accurate, but tedious.

Direct Fusion Methods for Chromium suitable for High Chromium Alloys.—Alloys containing more than 30 per cent. of chromium are not attacked by hydrochloric acid, and with alloys containing more than 8 per cent. chromium the latter metal is not completely dissolved. For such rich alloys direct fusion is preferable. For medium alloys a combined method is more satisfactory.

Ferro chrome requires very careful sampling. A large sample should be taken, and reduced by crushing and quartering. It is a brilliant silvery white, brittle, and often crystalline mass, and is very hard. Its reduction to fine powder is exceedingly troublesome. It must, however, be as fine as flour, being powdered first in a steel crushing mortar, sifted through a 90-sieve, and afterwards ground, a few grains at a time, in an agate mortar, 0.5 grm. being used.

Oxidising Mixtures.—Various oxidizing mixtures are employed.

I. Potassium nitrate (KNO_3) 2 parts, potassium carbonate (K_2CO_3) 1 part, and sodium carbonate (Na_2CO_3) 1 part.

II. Magnesia (MgO), sodium carbonate (Na_2CO_3), and potassium carbonate (K_2CO_3). This is known as tri-basic fusion mixture.

III. Caustic soda (NaHO) and sodium peroxide (Na_2O_2).

In using the first mixture, a little fusion mixture is melted on the bottom of the crucible, and the ferro chrome, previously mixed with ten times its weight of mixture, added and fused for about an hour, till completely decomposed.

In using the second mixture, the alloy is intimately mixed with

it, and heated for 2 hours in a muffle, when complete conversion to chromate is obtained.

With the third mixture, a few grammes of caustic soda is melted in a silver dish and the alloy added. Some sodium peroxide is then added, in small portions at a time, till complete oxidation has taken place, and the heating is continued for some time.

In either case the melted mass is boiled out with water, and dissolved in sulphuric acid. The solution contains chromates, manganates, and silicates, the iron being left as insoluble ferric oxide. The manganese is precipitated by addition from a burette of a saturated solution of permanganate (see p. 206), till a faint rosy colour appears. The precipitate is filtered off and washed. The liquor is then carefully acidified with hydrochloric acid and added to a solution of ferrous chloride, made by dissolving 2 grms. pure iron wire (99·8 per cent. Fe) in hydrochloric acid (see p. 176). The excess of iron is then estimated by standard potassium dichromate solution, and the excess deducted from the total iron added. The chromate produced by oxidation converts the ferrous into ferric chloride.

The amount of iron added must be in excess of that amount which the chromate in solution is capable of oxidizing.

These methods are suitable for ferro chrome and other high chrome alloys, but also yield good results on chrome steel (see also p. 213).

Estimation of Nickel.—The method followed is a modification of that given on p. 191.

From 0·5 grm. of steel high in nickel to 2·5 grms. of steel containing 2 per cent. or under is weighed out, dissolved in hydrochloric acid in a 20-oz. beaker, and evaporated in the beaker till pasty. The residue is dissolved in hot water, and made up to 150–200 c.c. without filtering. The solution is nearly neutralized with soda, and reduced by sodium sulphite, the excess of sulphite being carefully decomposed by hydrochloric acid, and sulphur dioxide expelled by boiling.* 10 grms. of sodium acetate is then added, and the hot liquid saturated with sulphuretted hydrogen.

Or the solution may be *neutralized* with soda (giving a slight precipitate), and reduced by sulphur dioxide, the excess being boiled off. Sufficient acetic acid is then added to the solution to convert all metals into acetates—about 15 c.c. Sulphuretted hydrogen is then passed through the warm solution till saturated, and about 10 grms. sodium acetate dissolved in the minimum quantity of water added.

The precipitate—a mixture of FeS and NiS—is allowed to settle, and

* This to prevent the subsequent precipitation of sulphur.

filtered as quickly as possible through a 12.5 c.m. filter. The filtrate should be colourless, but becomes yellow and often cloudy before filtration is finished. The precipitate is washed with hot boiled water, and the paper with the adherent precipitate put back into the beaker in which precipitation took place, and dissolved in boiling hydrochloric acid, with the careful addition of potassium chlorate in small portions at a time. The addition of potassium chlorate and boiling is continued till the liquor is quite clear and bright. Any sulphur that remains is removed, ignited in a porcelain crucible, the residue dissolved in hydrochloric acid, and added to the contents of the beaker. The solution is evaporated to small bulk to completely expel chlorine, and diluted to 50 c.c. The cold solution is neutralized with caustic soda, diluted to 150 c.c., 10–15 grms. sodium acetate added and dissolved. The liquid is then heated to boiling, when the iron is precipitated as basic acetate free from nickel. The cold procedure recommended here prevents contamination of the iron precipitate with nickel. The precipitate is filtered off and washed, or the solution is cooled, made up to 500 c.c., and 250 c.c. or other quantity filtered off (see p. 354). This quantity will, of course, represent a proportion of the original weight.

The nickel in this solution is then precipitated by addition of about 25 c.c. bromine water, and making alkaline with sodium hydrate. On heating to boiling, the nickel is precipitated as the black nickelic hydrate, which is filtered off, washed till free from alkali, dried, ignited, and weighed as NiO , or may be ignited in hydrogen and weighed as metallic nickel.

Copper, if present, is thrown down by the bromine. It is separated by dissolving the precipitate in hydrochloric acid, saturating the liquid with sulphuretted hydrogen, filtering and washing with sulphuretted hydrogen water. The solution is boiled till the sulphuretted hydrogen is expelled, then neutralized with soda and reprecipitated.

Silicon and tungsten must be removed by evaporation to dryness and filtering off, prior to proceeding with the nickel estimation. Nickel in ferro nickel may also be determined by the above methods.

Estimation of Tungsten.—The method depends on the reactions given p. 217; 1 to 2 grms. of the steel, in as fine a state of division as possible, is dissolved, with the usual precautions, in 50 c.c. nitric acid, sp. gr. 1.2, evaporated to dryness, and strongly heated for some time. The residue is taken up with 25 c.c. hydrochloric acid and evaporated to dryness, again dissolved and evaporated to very small bulk, diluted to 50 c.c., let settle completely, and decanted through a double filter

paper. The precipitate should not be disturbed if it can be avoided. The filtrate is rejected from time to time, after examining it to see that it is clear. The precipitate is then washed on the filter, and, if necessary, the washings refiltered till the filtrate is clear. It is then washed with 10 per cent. hydrochloric acid till free from iron, care being taken not to disturb the precipitate.

The residue is dried, ignited in a platinum crucible—with a little ammonium nitrate, if graphite be present—and weighed. The silica after determination must be deducted, and the difference is tungstic anhydride WO_3 , containing 79.3 per cent. tungsten. The silica may be removed by treatment with a little pure hydrofluoric acid, and careful evaporation to dryness; the loss is SiO_2 and the residue WO_3 .

Estimation of Vanadium in Steel (see p. 270). The solution of permanganate used for the estimation of iron may be employed, and the iron value of the solution multiplied by 0.9159 = vanadium present.

Estimation of Molybdenum.—The solution is prepared as for the estimation of phosphorus by ammonium molybdate (p. 356), an excess of sodium phosphate added, the solution warmed for some time, and the yellow precipitate collected and treated by Method 3, p. 273.

ANALYSIS OF SLAGS.

SLAGS vary so much in composition, according to the processes in which they are produced, that it is somewhat difficult to deal with them in a general manner. They are essentially silicates of metals, but fluorides, borates, chlorides, and other substances may be present in exceptional cases. Often, it is only necessary to determine a certain number of the constituents, which will depend on the operation from which the slag has been derived. The substances, the estimation of which is required and the proportions in which they exist, will determine the particular method to be followed.

Classification.—Slags are best classified by the proportions of silica and bases which they contain. The common classification into acid and basic slag is unsatisfactory. The best distinctions are based on the relative proportions of oxygen present in the bases and silica.

4RO	SiO ₂	or	4R ₂ O ₃	3SiO ₂	= sub	silicates	2 : 1
2RO	SiO ₂	„	2R ₂ O ₃	3SiO ₂	= mono	„	1 : 1
4RO	3SiO ₂	„	4R ₂ O ₃	9SiO ₂	= sesqui	„	2 : 3
RO	SiO ₂	„	R ₂ O ₃	3SiO ₂	= bi	„	1 : 2
2RO	3SiO ₂	„	2R ₂ O ₃	9SiO ₂	= tri	„	1 : 3

Most slags are either sub-, mono-, or bi-silicates or mixtures of these. Sesqui-silicates are occasionally present, but tri-silicates rarely. Increase in the proportion of silica, increases the refractoriness as well as the difficulty of decomposition for analysis. There is no fixed rule with regard to the solubility of any particular class of silicates, but speaking generally, those containing a larger proportion of bases are more readily decomposable.

In all cases, before proceeding to an analysis of slags of unknown character, the solubility in acids should be determined.

For analytical purposes they may be divided into—

I. **Insoluble slags.** Such as blast furnace slags, etc, and some lead and copper slags. These are usually almost insoluble in acids, and no separate determination of soluble matter is necessary.

II. **Soluble slags.** Such as tap cinder, basic slag, and others of a highly basic character.

General Scheme.—1. **Solubility in water.**—This is necessary in

slags containing alkaline bases and chlorides. Five grms. of the slag in an impalpable powder is treated with 50 c.c. of water and well boiled. After filtering, the liquid is evaporated to dryness in a weighed platinum basin, and the soluble matter determined.

2. **Solubility in hydrochloric or sulphuric acids.**

Determination of Insoluble matter.

3. **Analysis of insoluble slags or insoluble portion.**

4. **Analysis of soluble slags or soluble portion of those partially soluble.**

Insoluble Slags.—The determinations necessary may include SiO_2 , FeO , Al_2O_3 , CaO , MgO , Alkalies, MnO , Cr_2O_3 , CaF_2 , S, P, TiO_2 , and other metals.

Silica.—One grm. of the finely-powdered slag is mixed with 6 grms. of a mixture of sodium and potassium carbonates and a little nitre, in a platinum dish, fused, and treated as in analysis of ganister (see p. 379). The filtrate is reserved.

Alumina and Iron.—The filtrate from the silica, which should not exceed 250 c.c., is heated to boiling, made faintly alkaline with ammonia boiled and the precipitate filtered off. It is dissolved without washing, and the iron and alumina reprecipitated with ammonia, cooled, filtered, and washed. The two filtrates are mixed.

The precipitate is dried, ignited, and weighed as $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$. In a separate sample the iron must be separated and determined, as directed on next page, and the amount found deducted from the total weight. The amount of phosphoric anhydride found must also be deducted from the weight of the precipitate. Direct estimation of the alumina may be made as directed on p. 329, iron ores.

Where great accuracy is required, the alumina may be estimated as phosphate in the precipitate obtained by ammonia, by fusing the precipitate after weighing with 5 grms. pure potassium bisulphate in a platinum crucible and separating the alumina as directed for the estimation of aluminium in steel.

Estimation of Phosphoric Acid.—The ammonia precipitate, after weighing, is fused for a few minutes with pure caustic soda in a platinum crucible. The melted mass is dissolved in the minimum amount of hydrochloric acid and the estimation of the phosphoric acid effected by the molybdic, or combined processes, as described for Analysis of Steel (p. 356).

Lime and Magnesia.—The filtrate from the iron and alumina is evaporated, manganese removed as peroxide by bromine and ammonia (p. 353), or by ammonium sulphide, and the lime and magnesia estimated as in iron ores (p. 330).

Iron, Manganese.—3 to 5 grms. of the slag is fused in 20–40 grms. of sodium and potassium carbonates. The melted mass is extracted with water and hydrochloric acid, the iron peroxidized by nitric acid and precipitated by ammonium acetate, in the manner directed (p. 353), filtered, and washed. The filtrate contains the manganese. The precipitate is dissolved, neutralized, reduced and titrated with weak standard bichromate of potash solution. The iron, calculated to Fe_2O_3 , must be deducted from the total weight of the ferric oxide and alumina.

Manganese.—The filtrate from ammonium acetate is cooled, saturated with bromine, made alkaline with ammonia, boiled, and the precipitate filtered off and washed (see p. 330). The precipitate is transferred to a beaker and dissolved in the minimum amount of hydrochloric acid. This solution is evaporated with about 40 c.c. of strong nitric acid, and from 10 to 15 grms. of finely powdered potassium chlorate, added cautiously in small quantities at a time, the beaker being covered meanwhile. After boiling for a few minutes, till all chlorous fumes are expelled, the precipitate is allowed to settle, filtered and thoroughly washed. The precipitate is then added to a previously prepared solution of pure iron in sulphuric acid and shaken round till solution is complete. The excess of iron is estimated by titration with a standard solution of potassium bichromate (see pp. 177, 202, and 355). For every 0.1 gm. of manganese present, 0.204 gm. of pure iron in solution will be required. For ordinary slags 0.75 gm. and for manganiferous slags 2.5 grms. of pure iron is taken.

Alkalies.—1 gm. of the finely powdered material is mixed with 6 grms. of pure calcium carbonate and 1 gm. of pure ammonium chloride, the mixture placed in a platinum crucible, and heated to redness in a muffle for 1 to 1½ hour. The effect of this treatment is to decompose the complex silicates in which the soda and potash are combined and to partially convert the lime into silicate, and the alkalies probably into chlorides. After cooling, the crucible and its contents are boiled with dilute hydrochloric acid, the crucible removed and washed, and the solution carefully evaporated to dryness. The residue is moistened with hydrochloric acid, again evaporated to dryness, and gently ignited. It is then taken up with dilute hydrochloric acid, and the silica filtered off and washed. The filtrate is made alkaline with ammonia, boiled, and ammonium carbonate added to precipitate the lime. After boiling, 10 c.c. of ammonium oxalate solution is added to complete the precipitation of the lime. The precipitate, after settling, is filtered off and washed.

The filtrate from the lime containing magnesia, and the alkalies, together with the ammonium salts used in the precipitation, is evaporated

cautiously to dryness with the addition from time to time of strong nitric acid. In all, about 30 c.c. of strong nitric acid will be required. (This evaporation should be conducted in a well-used porcelain dish, or one that has been repeatedly boiled with hydrochloric acid.) By this means the ammonium salts are got rid of by conversion into nitrate and decomposition of the nitrate by heat. The residue is then dissolved in hydrochloric acid, the solution transferred to a weighed platinum dish, carefully evaporated to dryness, and after cooling in a desiccator, rapidly weighed. This must be done quickly in a dry balance case, as the chloride of magnesium is hygroscopic. The increase in the weight of the dish is the alkalies and magnesia as chlorides.

The residue is dissolved in the minimum quantity of distilled water, free from chlorides, by gentle heat. Strong ammonia, free from chloride, is added in large excess, and then about 10 drops *ammonium* phosphate solution to precipitate the magnesia. After standing for 12 hours, the liquor is filtered through a small filter, and the magnesia determined as pyrophosphate (see p. 358), due allowance being made for the volume of the original filtrate. The magnesium found calculated to $MgCl_2$, and deducted from the total weight of the mixed chlorides gives the weight of mixed chlorides of sodium and potassium. In the filtrate and washings the chlorine is determined gravimetrically or volumetrically with silver nitrate (see p. 307).^{*} From the total chlorine found, sufficient is deducted to combine with the magnesium, the weight of the magnesia phosphate being multiplied thus : $W \times 0.21614 \times 2.95$, and the result deducted from the chlorine found. The remainder of the chlorine was in combination with the alkalies. It should correspond with the quantity calculated from the weight of the mixed alkaline chlorides. The weight of the chlorides is calculated into oxides, *i.e.* K_2O and Na_2O , by multiplying the weight of chlorine found by 0.4495[†] to convert it into the oxygen equivalent, and adding this to the potassium and sodium actually present, as determined by the difference in weight, between the mixed alkaline chlorides and the chlorine they contain.

It is not usual to separate the alkalies from each other. But, if this be necessary, the process is modified after separating the magnesia. The liquor is slightly acidified with acetic acid and 2 or 3 c.c. of ferric chloride solution added. On heating to boiling, the phosphoric acid and iron added are precipitated as phosphate and basic acetate of iron. After filtering and washing the precipitate, the filtrate is again boiled down to dryness with strong nitric acid to expel ammonium salts, the residue

^{*} Factor for Cl in silver chloride = 0.24729.

[†] $\frac{O}{Cl} = \frac{15.96}{35.5} = 0.4495$.

moistened with hydrochloric acid, again evaporated to dryness, gently heated, and weighed.

To separate the potassium the residue is dissolved in the smallest possible quantity of water, an excess of platonic chloride added, and carefully evaporated on a water-bath nearly to dryness. Weak solution of platonic chloride and alcohol is added to dilute it, and the yellow precipitate ($2\text{KCl}, \text{PtCl}_4$) filtered off through a very small filter, washed with platonic chloride, and finally with alcohol, washing the precipitate to the centre of the paper. After drying at 100° , it is detached and weighed in a crucible. The paper is then burnt. Any precipitate adhering to it is decomposed, and yields $2\text{KCl} + \text{Pt}$. The ash is added to the contents of the crucible, which is then reweighed. From this increase the ash of the paper is deducted and the difference calculated to $2\text{KCl}, \text{PtCl}_4$ by multiplying by 1.4183 , *i.e.* $\frac{2\text{KCl}, \text{PtCl}_4}{2\text{KCl} + \text{Pt}}$ which, added to the weight of the portion detached from the filter, gives the weight of potassium chloroplatinate. Factor for $\text{K}_2\text{O} = 0.1939$. The sodium is taken by difference.

Titanic Oxide. (*See* Titanium.)

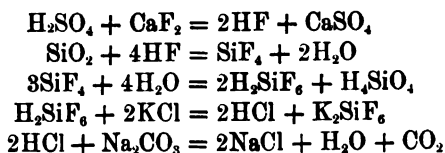
Chromic Oxide.—The slag is fused with the mixture of nitre, and carbonates of soda and potash, given p. 365, and the melted mass boiled out with water. The solution contains all the chromium, and some of the manganese. If it be purple, a few drops of alcohol are added to the hot solution to decompose the permanganate. The solution is acidified with sulphuric acid, ferrous sulphate solution—freshly prepared from pure iron—added, and the excess of ferrous salt estimated by titration with standard bichromate of potash.

Since the chromium present in the slag is converted into chromate by the fusion and into bichromate by acidification on adding a solution containing iron in the ferrous condition, the following reaction occurs: $6\text{FeCl}_2 + 14\text{HCl} + \text{K}_2\text{Cr}_2\text{O}_7 = 3\text{Fe}_2\text{Cl}_6 + 7\text{H}_2\text{O} + 2\text{KCl} + \text{Cr}_2\text{Cl}_6$ and hence, since $336 \text{ Fe} = 104.8 \text{ Cr}$., the amount of iron oxidized, *i.e.* the difference between the amount added and that found by titration with bichromate multiplied by $0.3119 = \text{Cr}$. or $0.4522 \text{ Cr}_2\text{O}_3$.

Sulphur.—1 to 2 grms. of the slag is fused with 10 of the nitre and potassium and sodium carbonate fusion mixture. The melted mass is extracted with water and hydrochloric acid, the silica separated by evaporation,* and the sulphur estimated as barium sulphate (see p. 277).

* In the presence of barium, as in some manganiferous iron slags, or lead, the fused mass must be extracted with water alone.

Estimation of Fluorides in slags from smelting chrome iron and lead.—This is based on the following reactions—



5 to 10 grms. of the slag, in a fine state of division, is weighed into a 150 c.c. flask (A, Fig. 95), a few fragments of quartz added, and covered with 40 c.c. strong sulphuric acid. The flask is closed

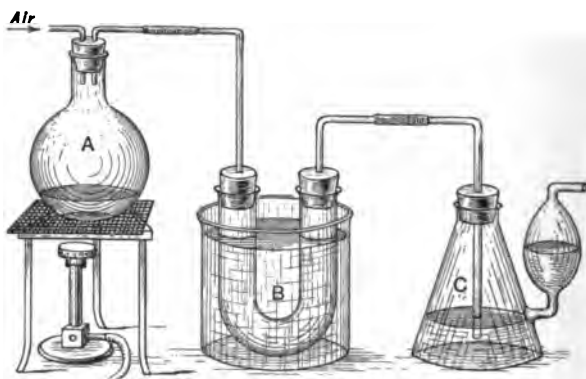


FIG. 95.

with a doubly perforated cork provided with two leading tubes. One tube communicates with a gas-holder (see Fig. 90), the other with the absorbing tubes. B is an empty U-tube, or condenser, cooled in a beaker of water to arrest acid fumes, C a set of nitrogen bulbs containing a strong potassium chloride solution mixed with an equal bulk of alcohol.

The flask is carefully heated to about 180°C ., and a very gentle stream of air passed through the apparatus. In from one to two hours decomposition is complete. The apparatus should be shaken from time to time. When the action is complete, the absorption bulbs are washed out into a beaker with alcohol and a little water, any gelatinous silica which adheres being detached. The hydrochloric acid liberated as above is titrated with a standard solution of sodium carbonate, using methyl orange as indicator. The standard soda must be made with a mixture of alcohol and water in equal parts. 53 grms. of pure dry

sodium carbonate is dissolved as directed and made up to a litre. The calculation is as follows :—

1 c.c. = 0.053 grm. Na_2CO_3

Na_2CO_3 is equivalent to 3CaF_2 . See equations

∴ the quantity of soda consumed multiplied by

$$\frac{3\text{CaF}_2}{\text{Na}_2\text{CO}_3} = 2.2075 = \text{CaF}_2$$

from which the percentage in slag can be calculated.

NOTE.—In substances other than slags, silica must be added. When chlorides are present, the hydrochloric acid generated must be removed by passing the gas before absorption through a tube filled with pumice that has been saturated with copper sulphate solution, and heated till *perfectly* anhydrous.

Copper in Slags may be estimated either colorimetrically, by cyanide, or by thiosulphate (see pp. 80–91), after fusion with alkaline carbonates and a little nitre to decompose slag.

Bismuth is estimated as oxide. The slag is fused with alkaline carbonates, the melted mass dissolved in hydrochloric acid, filtered, the solution made alkaline with ammonia, boiled, and the precipitate filtered and washed. It is dissolved in hydrochloric acid, the solution saturated with sulphurous acid, the excess expelled by boiling, and the liquid saturated with sulphuretted hydrogen. The mixed sulphides are collected, washed, dissolved in nitric acid, and the lead precipitated by evaporation with sulphuric acid. The solution is diluted slightly, so as not to precipitate the bismuth, and the lead sulphate filtered off. The bismuth in the filtrate may be precipitated by ammonia and ammonium carbonate, the precipitate filtered off, dried, ignited, and weighed.

NOTE.—In slags containing tin or antimony, the precipitate with sulphuretted hydrogen should be digested with yellow ammonium sulphide, filtered, and washed.

Lead Slags.—In slags free from sulphur, the metal may be determined as sulphate by precipitating the solution obtained by dissolving the mass obtained by fusion with alkaline carbonates and nitre with sulphuric acid. (*See Lead Assay.*)

In slags containing sulphide of lead or other metallic sulphides, or barium sulphate, the metal may be determined by decomposing from 0.5 to 5 grms. of the slag by acids or, if necessary, by fusion, as above. The solution obtained in either way is, without filtering, evaporated to dryness with nitric acid. Sulphuric acid is then added, and the solution evaporated to small bulk to expel nitric acid. It is diluted to 100 c.c., the residue is filtered off, washed, and washed into a beaker with about 100 c.c. of a saturated solution of sodium thiosulphate. This is kept at 60° to 70° C., not higher, for an hour or more, and afterwards filtered

and washed with thiosulphate solution. Lead sulphate is soluble in sodium thiosulphate; barium and calcium sulphates are not. The lead in the solution is precipitated as sulphide by sulphuretted hydrogen, filtered and washed, converted into sulphate, and weighed (see p. 64).

Tin.—For tin in tin slags, see p. 231. In other slags the estimation is conducted as follows: 2 to 5 grms. of the slag is fused with 10 to 25 grms. of a mixture of sodium and potassium carbonates, boiled out with water and hydrochloric acid, and evaporated to dryness, to render silica insoluble, in the usual manner. The residue is taken up with 20 c.c. hydrochloric acid, diluted and filtered, and the insoluble matter washed. The filtrate and washings are concentrated by evaporation to 100 c.c., saturated with sulphur dioxide to reduce iron salts present, the excess boiled off, and then made strongly alkaline with caustic soda. A brisk stream of sulphuretted hydrogen is passed through the warm liquid to saturation, and, after dilution, the precipitate is filtered off and thoroughly washed. It contains the Pb, Bi, Cd, Zn, Fe, Mn, and the bulk of the Cu and Ni which may be present. The filtrate and washings are mixed. If the precipitate be very bulky, it is advisable to dissolve and reprecipitate it; the filtrate obtained being added to the original one. The filtrates are concentrated, if necessary, and then carefully acidified with hydrochloric acid, when sulphides of tin, arsenic, and traces of copper and nickel sulphides may be precipitated. After washing, the precipitate is washed down with 20–60 c.c. strong hydrochloric acid into a beaker and digested with the acid for some time. After dilution, any residue is filtered off, and the tin in the filtrate precipitated by evaporating with 25 grms. ammonium nitrate diluting to 150 c.c. and boiling. The precipitate is filtered, washed, dried, ignited, and the tin weighed as oxide.

Zinc.—After decomposing the slag by fusion, as above, the metal may be determined as directed on p. 236.

Nickel and Cobalt.—After fusion and solution, proceed as directed (p. 191).

Soluble Slags.—Tap cinder and other slags, consisting largely of ferrous silicate, are completely decomposed by long boiling with hydrochloric acid, and may be treated as an insoluble slag or as an iron ore.

Basic Slag.—(Bessemer or open hearth.)

Silica is determined on 1 gm. by solution in hydrochloric acid, and twice evaporating to dryness as directed for insoluble slags.

Iron and Alumina are determined as in insoluble slags, using 2.5 grms. of slag.

Manganese.—Two and a half grms. is dissolved in hydrochloric

acid, and the estimation made as in the solution of the melted mass from insoluble slags (see p. 371). Iron and manganese.

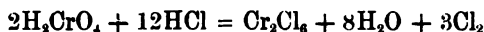
Sulphur is determined by the aqua regia process (p. 349).

Phosphoric Acid.—After removing silica, the phosphorus is estimated by the combined molybdate and magnesia methods (p. 359).

Lime and Magnesia are determined in the filtrate from the precipitation of iron and alumina with ammonium oxalate and phosphate respectively.

Chromium in Soluble Slags (Stead's Process).—Chromium is met with in slags from furnaces with chromite bottoms, sides, or parting courses.

Five grms. of slag is dissolved in hydrochloric acid, sulphurous acid added to the hot solution to reduce the chromate, 2 c.c. nitric acid added to peroxidize iron, and then made alkaline with ammonia, and boiled. The precipitate is collected on a filter and washed. It is then dissolved in dilute sulphuric acid, evaporated to small bulk, heated to boiling, and permanganate solution added till a permanent coloration is obtained. Strong hydrochloric acid is then cautiously added to the boiling liquid till the precipitated hydrated manganese dioxide is just dissolved. The liquid is then diluted to 150 c.c., and boiled till chlorine is expelled. No excess of hydrochloric acid must remain, or the chromic acid will be reduced thus—



The solution is added to a freshly prepared solution of ferrous sulphate in a 500 c.c. flask, and the excess of iron estimated by standard bichromate solution. The calculation is made as directed on p. 375.

ANALYSIS OF REFRACTORY MATERIALS.

CLASS 1. Acid. Including fire clay, ganister, silica bricks, and sand.

The technical examination of refractory materials, includes the tests for refractoriness, and also the chemical analysis of the material.

Refractoriness.—The capability of materials to resist high temperatures without fusion is determined in various ways.

Fire clay is ground, so that the whole sample will pass through a 30 or 40 sieve. It is then wetted with sufficient water to form a stiff plastic mass, and well kneaded. The cake is rolled out to a thin slab, about $\frac{1}{4}$ inch to $\frac{3}{8}$ inch thick, and a piece about $1\frac{1}{4}$ inch square

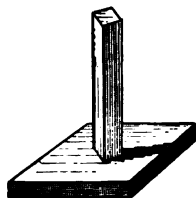


FIG. 96.

cut out. The edges of this piece are made as sharp as possible. Another piece, about $1\frac{1}{2}$ inch long and $\frac{3}{8}$ inch wide, is also cut with sharp edges, and attached to the middle of the square piece of clay by means of a little clay slip, so as to stand upright (see Fig. 96). The test piece is thoroughly dried and then placed in a Cornish crucible, resting on a little small coke. A lid is luted on* the crucible, and the whole exposed to the highest attainable temperature in a wind furnace for three hours. After cooling, the crucible is broken and the test piece carefully examined. Any softening that may have taken place will be made apparent by the rounding of the edges, fusion of any projecting particles on the surface and edges, and distortion of the pillar or base, or the partial or complete fusion of the clay.

The relative resistance offered to the corrosive effects of slags and fluxes may be determined by making some of the clay into a crucible in the mould (see Fig. 31), and, after carefully drying, baking it at a low temperature in a muffle. About 20–30 grms. of litharge is placed in the crucible, which is then strongly heated. The time which elapses before the crucible is perforated as compared with a clay of known character is a fair measure of the resistance to corrosion offered by the

* Lutes; see p. 168.

clay. At a yellowish heat, a crucible made from a good clay will resist for twenty minutes or longer. The resistance offered depends on the coarseness or fineness of the grain, as well as upon the composition of the clay. It is, therefore, important that the clays for testing and comparison should be passed through the same sieve. A severer test with a mixture of cuprous oxide and litharge may be made if desired. Since the liability of a crucible to crack when suddenly placed in, or removed from, a hot furnace, depends on the coarseness of the grain, this consideration must be borne in mind in reporting on clays. Coarse-grained crucibles are less liable to crack, but more liable to corrosion. The finer the grain the greater the care which must be exercised by heating the crucible gradually.

The determinations required in the analysis are—

1. Hygroscopic water (moisture).
2. Combined water and organic matter.
3. Free silica and insoluble matter.
4. Total silica.
5. Alumina.
6. Lime and magnesia.
7. Ferric oxide.
8. Ferrous oxide.
9. Alkalies.

In sand, ganister, silica and dinas bricks and steel casting sand, silica, iron, alumina, lime, and magnesia may be determined in the same sample.

Moisture.—The hygroscopic water is determined in the usual manner by drying in a water oven till the weight is constant.

Combined Water and Organic Matter.—Two grms. of the substance, dried at 100° C., is ignited for half an hour, in a strongly heated muffle in a platinum crucible, and, after cooling, re-weighed. The loss on ignition is reported as combined water and organic matter.

Insoluble Matter.—Two grms. of the material is boiled for some time with 20 c.c. strong hydrochloric acid, and, after dilution to 100 c.c., filtered, washed, dried, ignited, and the residue weighed.

Silica.—Two grms. of the sample (in the finest possible state of division), dried at 100° C., is mixed intimately with 10 grms. of a mixture of equal parts of sodium and potassium carbonates, and a little potassium nitrate—about 1 gm.—and placed in a platinum crucible or dish. The mixture is fused for some time in a hot muffle or over the foot blow-pipe. After cooling, the melted mass is boiled out with water in a large porcelain basin. The crucible and cover are removed, washed, by a little hot dilute hydrochloric acid sprayed on them from

a wash-bottle. The melted mass is now cautiously dissolved in hydrochloric acid poured down the side. It is best to cover the dish with a large funnel, supported over it by means of a clamp. When the carbon dioxide is completely expelled, the funnel is washed and removed, and the liquid evaporated to complete dryness on a water-bath. Unless a water-bath be used, the solution will require constant stirring when reduced to small bulk, to prevent loss. When quite dry, the residue is moistened with 15 c.c. hydrochloric acid, and again evaporated to dryness. The final heating must be effected over a naked bunsen or on the hot plate, but when dry the dish must be covered, to prevent the residue (containing large quantities of sodium and potassium chlorides) from jumping out. The residue is moistened with hydrochloric acid and again dried. It is then taken up with 20 c.c. hydrochloric acid, warmed, diluted to 150 c.c., and the insoluble silica filtered off, washed, dried, ignited, and weighed. It should be quite white.

The filtrate contains the bases. It is allowed to cool, made up to 500 c.c., or any other known volume, less than 500, if possible, and divided into two equal portions.

Iron. In one the iron is determined. The liquid is evaporated to small bulk, neutralized with soda, reduced with sulphurous acid, excess boiled off, and the solution titrated with a very dilute standard solution of potassium bichromate.

Alumina. In the other the alumina is determined by the method given on p. 329, Analysis of Iron Ores. The filtrate is reserved for the lime and magnesia.

NOTE.—In the analysis of fire clays a quarter of the solution (0.5 grm.) may be taken for the estimation of alumina, or the precipitate will be too bulky.

Alternative Method for Iron and Alumina.—Only 1 grm. of the substance is taken for fusion. The whole of the filtrate from the silica is carefully precipitated by ammonia, boiled, and the iron and aluminium hydrates collected on a filter, washed, dissolved in hydrochloric acid, reprecipitated by ammonia, filtered, and the filtrates mixed and reserved. The precipitate is dried, ignited, and weighed in a platinum crucible, as $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$. The weighed precipitate is dissolved by digesting in hydrochloric acid, the iron reduced by sulphurous acid, and estimated by a dilute standard bichromate of potash solution. The amount of iron found calculated to Fe_2O_3 , * and deducted from the total weight of the precipitate gives the weight of Al_2O_3 .

The solution of the ignited precipitate is difficult, but is rendered easier by grinding it in an agate mortar and re-weighing to determine

* $\times 1.4286$.

the amount lost. It may also be dissolved by fusion with 5 grms. of pure potassium bisulphate for fifteen minutes, and boiling out the fused mass with water and 5 c.c. of sulphuric acid, after which the estimation of the iron is proceeded with as above.

Or the separation of the iron and alumina in the precipitate may be effected by transferring the weighed precipitate to a porcelain boat and heating it in a current of pure hydrogen. The loss in weight is the O in combination with the iron.

$$\text{Fe}_2\text{O}_3 + 3\text{H} = 3\text{H}_2\text{O} + \text{Fe}_2$$

$$\therefore \text{loss} \times \frac{111.8}{47.88} = \text{Fe and loss} \times \frac{159.68}{47.88} = \text{Fe}_2\text{O}_3$$

This may be deducted from the original weight of the precipitate. Confirmation must be made by dissolving the residue in hydrochloric acid, which is easily effected after heating in hydrogen, and titration.

Ferrous and Ferric Oxides. (*See Iron Ores.*)

Lime and Magnesia.—These are estimated in the filtrates from iron and alumina, in the manner detailed on p. 330.

Alkalies are estimated as described for Slag (p. 371).

CLASS 2. Basic Refractory Materials.—Including lime and limestone, magnesia and magnesite, dolomite, bauxite, chromite, and basic bricks.

Analysis of Lime and Limestone. Magnesia, Magnesite, and Dolomite.—The following determinations are necessary :—

Moisture.

Loss on ignition.

Carbon dioxide.

Silica and insoluble matter.

Iron.

Lime.

Magnesia.

Alkalies.

Sulphur and Phosphoric acid.

Manganese and zinc may also be looked for, and occasionally a detailed analysis of the insoluble matter is required.

Moisture and loss on ignition are determined as described for clay (p. 379); **carbon dioxide** by loss, as described for iron ores (p. 332); **insoluble matter**, as for iron ores (p. 329).

Iron, Lime, and Magnesia.—One grm. of the substance is taken, dissolved in hydrochloric acid, diluted to 100 c.c. and filtered. The residue is washed and the filtrate reserved for the determination of the iron, lime, and magnesia by the methods used for iron ores. The iron,

is precipitated by ammonia and determined by volumetric methods. Lime is precipitated from the filtrate as oxalate and weighed as oxide. Magnesia is estimated in the filtrate as phosphate.

In magnesite the iron must be separated by a double precipitation, first with ammonia, and after solution of the precipitate in hydrochloric acid with ammonium acetate, and the filtrates mixed. The precipitate first obtained will be contaminated with magnesia.

Alkalies.—These are determined by heating 10 grms. of the material with 1 grm. of pure ammonium chloride, and proceeding as directed on p. 371.

Manganese, if present, is determined on 10 grms. of the material. After solution in hydrochloric acid, the liquid is diluted and filtered, and the iron removed as basic acetate (p. 353). In the filtrate the manganese is precipitated by bromine.

Phosphoric Acid.—This is present as phosphates of iron and calcium. 5 to 10 grms. of the finely powdered substance is dissolved in hydrochloric acid and evaporated to dryness, moistened with hydrochloric acid, and again evaporated to dryness. The residue is taken up with hydrochloric acid with the aid of heat, a few drops of nitric acid added, boiled, the liquid diluted to about 150 c.c., and a slight excess of ammonia added. This throws down the hydrates of iron and aluminum, and the calcic phosphate, etc. The solution is boiled for about 10 minutes, filtered, and the precipitate thoroughly washed. 5 c.c. warm hydrochloric acid (heated in the beaker in which the precipitation took place) is poured over the filter to dissolve out the hydrates and phosphates, and the insoluble residue is well washed. The filtrate is then made alkaline with ammonia, the precipitate dissolved in nitric acid, and the phosphorus estimated by precipitation with ammonium molybdate, as directed for steel (see p. 356). The result must be expressed as P_2O_5 . Factor = 0.0373.

Sulphur.—This element is often determined by the aqua regia method, as directed for steel.

NOTE.—In the determination of sulphur the total amount present can only be estimated by fusion with pure sodium carbonate and nitre, as directed (see p. 276). This is especially necessary in the analysis of limestone and dolomite employed in connection with basic steel manufacture.

Analysis of insoluble matter.—This is carried out as directed for Insoluble Slags and Acid Refractory Materials (p. 370).

BAUXITE.—The determination of moisture, loss on ignition, insoluble matter, carbon dioxide, and the examination for sulphur and phosphorus are carried out as above.

Silica.—Most bauxites contain titanic acid, TiO_2 , which remains

with the silica obtained in the analysis. The silica is determined by fusing 1 gm. of the substance with 6 grms. of a mixture of sodium and potassium carbonates. After extracting the melted mass with water and hydrochloric acid, and determining the silica, as in the analysis of acid refractory materials, the silica and titanic oxide are fused with potassium bisulphate, and treated as directed on p. 216.

Iron and Alumina.—The filtrate from the insoluble matter is made up to 200 c.c. The iron is determined in 100 c.c. of the filtrate (= 0.5 gm. bauxite), and the alumina in 50 c.c. (= 0.25 grms.), by the method given for acid refractory materials.

FUEL.

Examination of Coal.—The technical examination of coal includes the following determinations :—

Specific gravity.
Moisture.
Ash.
Coke.
Volatile matters.
Fixed carbon in coke.
Sulphur.
Chlorine.
Calorific power.

Specific Gravity.—This may be determined by the ordinary methods of weighing, first in air, and afterwards, immersed in water suspended by a hair. $\frac{\text{Wt. in air}}{\text{loss of wt. in water}} = \text{sp. gr.}$, or better, by means of the sp. gr. bottle (Fig. 97). This method admits of the coal being

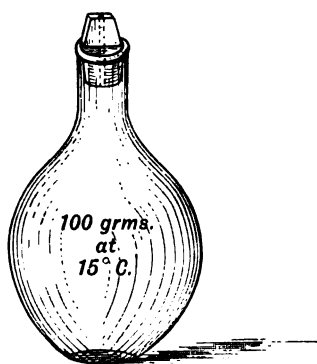


FIG. 97.

powdered, and a better sample being obtained. The bottle contains 100 grms. of water at 15° C. 2 to 3 grms. of the coal are weighed into it, covered with water, and the coal allowed to soak till saturated. The bottle is then filled up with water at the standard temperature, the stopper inserted, carefully wiped dry and re-weighed.

W = wt. of coal in air.

F = wt. of flask filled with water.

F₁ = wt. of flask + water + coal.

$$\text{then Sp. gr.} = \frac{W}{W + F - F_1}$$

Moisture.—This is determined by heating 2 grms. of the finely powdered coal spread out on a watch-glass, in the water-bath at 100° C.

for 1 hour. If the sample be heated for too long a time, in some cases there is loss other than water, and in other cases a slight gain in weight due to oxidation.

Ash.—Two grms. of the powdered coal is weighed out, placed on a porcelain dish, and carefully heated in a muffle till all carbonaceous matter has been burnt off. The residue is brushed on to a weighed watch-glass and carefully weighed. Care must be taken to heat gradually, as some coals decrepitate strongly, and loss would be occasioned. The colour of the ash is some indication of the nature of the inorganic matter present. A red colour is due to ferric oxide, and usually indicates the presence of pyrites, a white ash being generally produced in its absence. Platinum vessels should not be used for this purpose. The ash of coal varies generally from 2 to 14 per cent., but the latter figure is often exceeded.

Analysis of Coal-ash.—This may be conducted in the same manner as an analysis of fire clay. Sulphur (as sulphuric acid) in the ash must be determined by fusion with nitre and pure sodium and potassium carbonates (see p. 331).

Coke.—Coke is best determined by placing 5 grms. of the powdered coal, passed through a 40 sieve, in a porcelain crucible provided with a lid. The crucible and its contents are then placed inside a larger pot, packed in fragments (not powdered) of coke or charcoal, and covered with coke and a lid (Fig. 98). Crucibles of the same size should always be used, and as far as possible the coke fragments should be uniform. The crucible is then placed in a wind furnace and heated strongly for 1 to 1½ hour till all volatile matter is expelled. It is then removed from the furnace, and after cooling, the porcelain crucible is carefully removed, and its contents weighed* and afterwards examined. The residue may be (a) pulverulent; (b) slightly fritted; (c) coked, spongy, and swelled; (d) strongly coked, and compact.

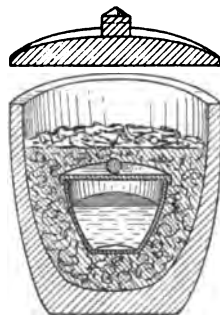


FIG. 98.

A pulverulent coke, if in small quantity, not exceeding 60 per cent., indicates that the coal is a non-caking coal, rich in oxygen or the least altered form of bituminous coals. If the quantity be much less, it is probably a lignite, and should be carefully examined. If the coke is pulverulent but the amount exceeds 80 per cent., the coal is of an anthracitic character, if not a true anthracite, *i.e.* is one of the most

* The carbon round the crucible must be disregarded. It results from the decomposition of escaping hydrocarbons by contact with the hot porcelain surface.

highly altered forms, containing little oxygen or hydrogen. A slightly fritted coke indicates that the coking property is not strongly developed. Spongy coke, full of holes, moderately difficult to break up, which has swelled so as to flatten itself against the lid of the crucible, indicates that the mass has been in a pasty or semi-fused state. Such coals are highly caking, but do not yield the densest coke. Compact coke, as in the former case, takes the internal form of the vessel, but there is little or no swelling, and the coke is not spongy. It is usually large in quantity, and it is yielded by good coking coals.

Volatile Matters.—This determination is made by deducting the moisture from the loss of weight on coking.

Fixed Carbon.—The coke obtained consists of the non-volatile carbon and the inorganic residue or ash.*

As the ash is so variable in quantity, the weight of coke is not a safe indication of the amount of carbon present. The fixed carbon is obtained by deducting the percentage of ash from the percentage of coke obtained, thus—

Ash in coal = 7.56 per cent.

Coke found = 68.74 „

Fixed carbon in coke : $68.74 - 7.56 = 61.18$

Or the coke may be placed on a scorifier in a muffle, heated till all carbonaceous matter has burnt off, and the residue weighed and deducted from the weight of coke.

Sulphur.—The sulphur in coal exists as (1) organic sulphur, *i.e.* in combination with the organic matter; (2) as iron pyrites and occasionally other sulphides; and (3) as calcium, aluminum, and other sulphates. Usually only total sulphur is determined, but the sulphur in the ash may generally be taken as that existing as sulphates.† The organic sulphur is only a minute quantity.

Total Sulphur.—One or two grams of the finely powdered coal is mixed with two or three times its weight of a mixture of two parts pure MgO and one part Na_2CO_3 , a little more being used as a cover.‡ The mixture is placed in a porcelain dish and heated to redness in a muffle for from $\frac{3}{4}$ to 1 hour, till the carbonaceous matter is completely burnt off. Occasional stirring with a platinum wire towards the end will ensure complete combustion. During the heating the sulphur is converted into sulphur dioxide, which, with the lime and oxygen, forms

* Less some small proportion of sulphur, which is volatilized. It may be disregarded.

† In coals containing carbonate of lime some of the sulphur found in the ash may have been retained from the pyrites present by the lime resulting from the decomposition of the carbonate while burning off the carbonaceous matter.

‡ Or 1 gm. of coal is mixed with 8 grms. KNO_3 , 4 grms. K_2CO_3 , and 16 grms. $NaCl$, and gently heated till quietly fused in a platinum crucible.

calcium sulphate. After cooling, the contents of the dish are carefully transferred to a beaker containing 150 c.c. of water and about 1 c.c. of bromine, or some bromine water is added. The whole is then cautiously dissolved in hydrochloric acid, heated to boiling, and the residue filtered off and washed. The filtrate is nearly neutralized with ammonia, heated to boiling, and the sulphate precipitated by a hot solution of barium chloride, boiled for about 10–20 minutes, filtered, washed, dried, ignited, and weighed. Factor for sulphur = 0.1874.

NOTE.—A blank determination should be made, using the same quantities of lime and other reagents as are actually employed. If any sulphate be precipitated it must be deducted from that found in the analysis.

Chlorine.—This element is not generally estimated, but is nevertheless of great importance where the products of combustion come into contact with copper and brass boiler tubes. Ten grms. of the coal is mixed with 20 grms. of soda lime, or pure lime, and carefully ignited at a dull red heat in a muffle till the whole of the carbonaceous matter is burnt off. The residue is extracted with water (or dissolved in pure nitric acid), filtered, and the chlorine estimated gravimetrically by precipitation with silver nitrate. The silver chloride, after boiling and settling, is filtered, washed, dried, and treated as described (p. 307).

Phosphorus.—Phosphorus in coal is determined in the ash. One grm. of the ash is fused with 5 grms. of sodium and potassium carbonates. The melted mass, after extraction with water and hydrochloric acid, is twice evaporated to dryness with hydrochloric acid. The residue is taken up with hydrochloric acid, a drop or two of ferric chloride added, and the solution made alkaline with ammonia. The precipitate is collected, washed, and the phosphoric acid in it determined by the combined method given for Iron (p. 359).

Calorific Power.—For practical purposes this is determined by means of the calorimeter, designed by Lewis Thompson * (Fig. 99).

The apparatus consists of a glass vessel (A), containing, when filled to the mark, 29,010 grs. of water (see below). Some instruments are graduated in grams, and 2000 grms. of water are employed. The copper cylinder (B) forms the furnace, in which the coal, previously mixed with the quantity of deflagrating mixture to supply the oxygen necessary for its combustion, is placed. The base (C) has a socket (D) for the reception of the furnace, and is furnished with three springs (E) to engage with the cover (F), a hollow copper cylinder with small perforations round the base, and a long narrow tube which rises above the surface of the water in (A) and terminating in a tap.

The determination is made as follows. Thirty grs., or 2 grms. of

* Bomb calorimeters of the Berthelot type are also used. See "Poole's Calorific Power of Fuel."

the coal, in the finest possible state of division, is weighed out and mixed with 300 grs., *i.e.* ten times its weight of a mixture of three parts of potassium chlorate and one part of potassium nitrate. With coke and anthracite, 360 grs. of mixture—*i.e.* twelve times its weight—is required. (This is the most useful mixture, but in some cases it is

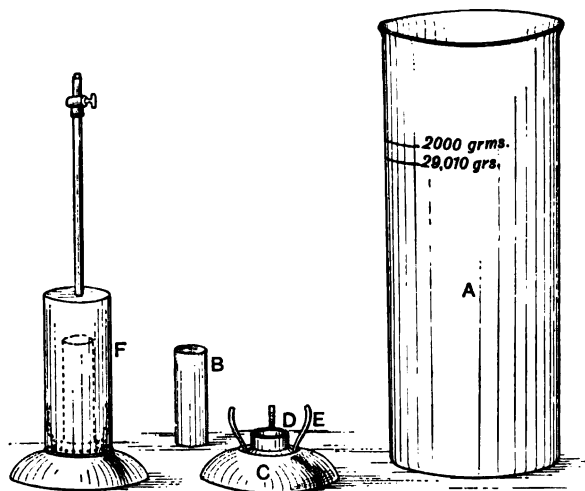


FIG. 99.

advisable to diminish the nitrate. This is indicated when fusion and incomplete combustion from that cause are encountered.) The mixture must be well made, finely ground, and dry. The coal and deflagrating mixture should be thoroughly mixed on glazed paper, afterwards ground together in a mortar in small quantities at a time, and the mixture transferred to the furnace tube. It should not be rammed, as is often advised, but should be shaken down by tapping the bottom of the furnace on the bench. The amount of mixture given will fill the tube of the standard apparatus. After placing the furnace in its socket, the end of a short length ($\frac{3}{4}$ inch) of fuse is inserted in a hole made in the top of the mixture by a wire. The fuse consists of a few threads of lamp-cotton, previously soaked in potassium nitrate, and allowed to dry. It should be kept in a dry place and tested previous to use. The end is embedded in the mixture.

The temperature of the water in the jar (previously filled) is then taken with a thermometer reading to 0.1° F., or 0.05° C., and should be from $5-7^{\circ}$ F. below the temperature of the room.

The tap of the cover cylinder is turned off, the fuse ignited, the cover

immediately slipped over the springs, and the whole lifted and placed in the water in the jar. Combustion begins as soon as the fuse burns down to the mixture, and is very vigorous. The gases generated escape through the holes at the base, and rise through the water. The combustion should occupy about 2 minutes. As soon as action ceases the tap at the top is opened, water enters the cylinder, and cools the furnace. By lifting the cover, etc., and inclining it, the hot water with which the furnace is filled may be emptied out, and by moving the cover up and down, the water may be thoroughly mixed. After this the temperature is again taken, the highest point reached being noted.

Experiment has shown that the average total loss of heat in this apparatus—consisting of heat carried off in the escaping gases, heat taken up in decomposing the salts, and by the apparatus, is about one-tenth of the total recorded, and this is added to the observed rise in temperature. Thus—

$$\begin{array}{rcl}
 \text{Temperature after combustion} & 63.8^{\circ} \text{ F.} & \\
 \text{,, before ,,} & 51.9 & \\
 & \hline
 & 11.9 & \\
 \frac{1}{10} \text{ added} & 1.19 & \\
 & \hline
 & 13.09^{\circ} \text{ F.} &
 \end{array}$$

With the given weights of water and fuel in grains, this represents the evaporative power of the coal. Since the latent heat of vaporization of water is 967 (British units) and $967 \times 30 = 29,010$ grs., it follows that each grain of fuel must give out 967 heat units to produce an increase of 1° , and the observed rise in T° represents the evaporative power. The *calorific* power may be calculated thus—

$$\frac{\text{Rise in } T^{\circ} \times \text{wt. of water}}{\text{wt. of fuel}} = \text{cal. power}$$

If F° are taken, these will represent British units; if C° , calories.

British units may be converted, for comparison, into calories by multiplying by $\frac{5}{9}$.

COKE.

The determinations generally made in the technical examination of coke are—

Ash.

Sulphur.

Calorific power.

Absorptive power to determine cell-structure.

Specific gravity.

Ash.—Sulphur.—These determinations are made as for coal, but in coke the amount of sulphur in the ash should be always determined.

Calorific Power.—In general, the weight of deflagrating mixture required will be 12 times that of fuel, and greater attention should be paid to grinding the charge finely.

Absorptive Power.—The determination of the absorptive power of the coke for water may be made by taking one or more sample pieces, and, after weighing, boiling in water for 2 hours, or longer, and allowing to stand till cold. The pieces are taken out, surface water removed, and the coke weighed. The increase in weight is due to the water taken up. It may be reduced to unity for comparison by dividing the weight of water by the weight of coke. The uniformity or otherwise of the structure must be carefully noted.

Specific Gravity.—The apparent specific gravity may be determined with sufficient accuracy for practical purposes by the usual method of weighing in water and air (p. 384).

GASEOUS FUELS.

The gases of which analyses are likely to be required in metallurgical work comprise flue gases, producer, and possibly water gas. For the analysis of other gases some special work on gas analysis must be consulted.

The constituents usually requiring determination are carbonic acid gas, CO_2 ; carbonic oxide, CO ; oxygen, O ; hydrogen, H ; and nitrogen, N . Sometimes the proportions of sulphur dioxide and sulphur trioxide may be required.

Flue and Producer Gases.—Producer gas consists of CO_2 , CO , H , N , and CH_4 . In the case of flue gases, free oxygen is also present.

Collecting the Sample.—The sample is best collected in a bottle, such as that shown in Fig. 101; or in tubes, Fig. 102.

Flues from which gas samples are to be withdrawn should be provided with a sampling hole stopped with a plug. Into this hole a perforated cork, somewhat charred, through which passes a glass tube, connected by rubber tubing with the collecting bottle, is inserted. The end of the tube inserted into the flue must be covered with asbestos, protected by copper-wire gauze, to keep out the dust, and to prevent the tubes becoming choked. In some cases, especially with wide flues, a tube closed at one end and having a slit along the side turned in the direction the gas is passing, which projects into the flue, is the best means of obtaining a fair sample uninfluenced by the cooling action

of the brickwork, or of accidental variations in composition, due to a multitude of minor causes. Such a tube is shown in Fig. 100. This



FIG. 100.

tube may, in some cases, be a fixture. The sample may be obtained by attaching the glass leading-tube to a sample bottle arranged like an aspirating bottle. Stead's gas sampler (Fig. 101) is employed for taking a sample of furnace gas during any length of time. A water-bottle is used as a mercury reservoir, its lower neck being connected by a stout rubber tube with the right-hand bottom cock of the sampler. By raising this bottle the sampler is filled with mercury. On lowering it, the mercury is allowed to run back into the upper neck of the reservoir-bottle, out of the left-hand bottom cock of the sampler, into which the gas is drawn from the furnace flue through the top left-hand cock.

The gas-holder shown on p. 339 also serves well, if care be taken that the tube leading from the reservoir above is always left full of water. Otherwise, when any of the gas is removed, by admitting water from the reservoir and opening the exit tap, the air contained in the tube will be carried down and mix with the gas.

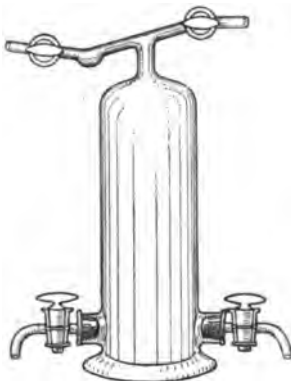


FIG. 101.

In both cases, when the gas issuing from the rubber tube connected with the flue tube has cleared out the air, it is slipped on to the elbow, and the lower tap opened. The bottle and elbow tube are completely filled with water, and as the water runs out the gas is drawn in. All connections must be gas-tight.

In the form figured 101, the gas is expelled for examination by attaching one of the upper branches to the apparatus for analysis, and the

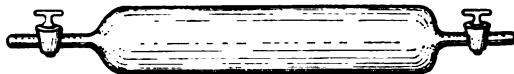


FIG. 102.

other, by means of a flexible tube, to a funnel containing water, which, on being admitted, expels the gas, if the other tap be opened.

For convenience of carriage, sampling tubes are often preferable.

Such tubes resemble a long pipette with a tap at each end (Fig. 102), the tubes of which are capillary. Each should have a capacity of 150 to 200 c.c., and several are filled. They may be filled with gas, by first filling them with water, connecting one end to the tube in the sampling hole, and allowing the water to run out. A better method is to fill each separately by means of an indiarubber aspirator or pump,* such as is seen on the Orsat apparatus (N, Fig. 103). A few moments' pumping will completely exhaust the air and fill the tube with gas. The taps being turned off, this may be removed for examination. The gas is expelled by attaching one end of the tube to the analysis apparatus, and placing the other end under water in a deep vessel; on opening the taps water will enter and expel the gas.

For technical purposes the gas may be analyzed by means of the Orsat Lunge apparatus (Fig. 103). The apparatus consists of a graduated

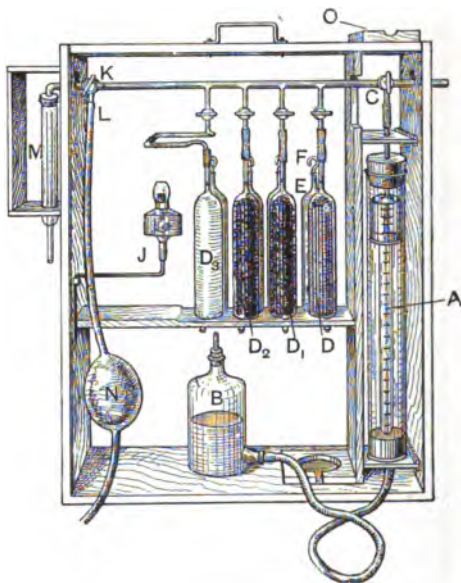


FIG. 103.

gas burette, A, surrounded by an outer glass cylinder, forming an air-jacket to prevent the gas being affected by fluctuations of temperature. The burette, A, is connected at the bottom with a water-bottle, B, by means of a stout rubber tube furnished with a clip. The top of the burette communicates by means of a capillary tube, C, with a series of four pipettes, one of which is shown separately (Fig. 104). Each pipette is

* Or Fletcher's aspirator.

provided with a glass stop-cock, so that by elevating the bottle, B, the gas in A may be driven over into any of the pipettes as desired, the water rising in A and taking its place. In the bulbs of these pipettes the various constituents of the gases are absorbed by suitable solvents in the following order, CO_2 , O, CO, leaving a mixture of H, CH_4 , and N, which will be dealt with subsequently. The bulbs, D, D_1 , D_2 , in connection with the cross-tube, C, are filled with small glass tubes, which, by being wetted with the solvent, increase the surface exposed by the absorbing liquid employed. The second bulb of each pipette (E, Fig. 104), in connection with

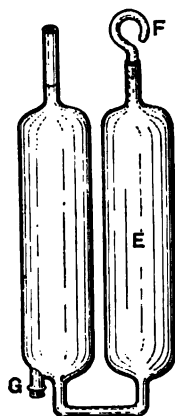


FIG. 104.

D, is a reservoir into which the liquid passes when displaced by the introduction of the gas. The tube, F, ends in a small aperture, by which it communicates with the air. The opening, G, is for cleaning purposes, and the removal of the liquid. The three pipettes immediately following the burette are identical in form, and serve for the removal of the CO_2 , O, and CO respectively. The fourth pipette is connected in a somewhat different manner by means of the bent glass tube, H (see also Fig. 105), attached to the branch from the capillary tube, C, and the

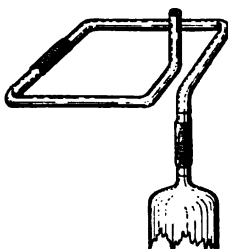


FIG. 105.

pipette, D_3 , by means of rubber tube. Under this tube is a small spirit-lamp, J. The pipette contains only water. Its object will be made clear in dealing with the estimation of hydrogen. K is a three-way tap by which the gas burette, A, may be put in connection with the air through L, or connection established with the U-tube, packed with cotton wool to filter off dust, and through which the burette is filled. N is an indiarubber bulb aspirator used for drawing the liquids in the pipettes up to the mark on the stem. O is a rest for the bottle, B, when lifted.

Before charging the pipettes, detach one, and fill the bulb at the back with water to determine its capacity. Then suck the water into the front bulb. It should be sufficient to completely fill it, and leave enough in the bulb behind to cover the connecting tube.

Charging the Pipettes.—The first pipette is for the purpose of removing CO_2 , and is charged with a solution of potash, made by dissolving 1 part of caustic potash in 3 of water. This must be kept in a well-stoppered bottle, and the pipette recharged when the absorption becomes slow.

The second bulb is employed to absorb the oxygen, and is charged with a solution made as follows: 25 grms. of pyrogallie acid are dissolved in 100 c.c. water, and 150 c.c. of a strong solution of caustic soda, 1 part caustic soda in 3 parts water, added.

In the third bulb the carbonic oxide, CO, is absorbed by a solution of ammoniacal cuprous chloride. This is prepared by dissolving 250 grms. of ammonium chloride in 750 c.c. of water in a beaker, and carefully adding to the hot solution 250 grms. of cuprous chloride (Cu_2Cl_2). After cooling, 85 c.c. of ammonia of sp. gr. 0.904 is added. This may be made by adding 4 volumes of 0.880 ammonia to 1 of water.

The cuprous chloride solution may also be made by dissolving 170 grms. of cupric chloride in water, and adding 68.5 grms. of precipitated copper. The ammonium chloride is then added in the solid state, and gently heated till the whole is dissolved. A few drops of hydrochloric acid may be added. When completely dissolved, the solution is diluted to 750 c.c., and the ammonia added as before. This solution must be kept carefully. Copper should be placed in the bottom of the bottle.

This solution, as well as absorbing CO, takes up the ethylene and other heavy hydrocarbons. The quantities of these in the gases usually examined by metallurgical chemists are so small that they may be neglected. If their determination is necessary, some treatise on gas analysis may be consulted.

The fourth bulb is filled with water only. The connecting tube contains a thread of palladiumized asbestos, as devised by Hempel, whose instructions for its preparation, slightly modified, are as follows: 0.1 gm. of palladium is dissolved in aqua regia, and evaporated to dryness on a water bath. The residue is dissolved in a little water, and a few c.c.s of a saturated solution of sodium formate added. A slight excess of Na_2CO_3 is then added, and the liquid evaporated to small bulk. About 1 gm. of finely fibrous asbestos, previously combed out, is placed in the liquid, and absorbs the whole. It is carefully dried and gently heated. Palladium is precipitated on the asbestos. Water is added, and the asbestos cautiously washed to remove sodium salts, and then dried. It contains over 3 per cent. of palladium. When gently heated, the spongy metal causes the combination of a mixture of H and excess of O quietly. Some of the asbestos is twisted into a thread somewhat thicker than sewing cotton. A length of 4-5 cms. is cut off and slipped into the capillary tube, H, 1 mm. in diameter before bending. This is best done by inserting the thread in the tube, putting the end under water, and gently drawing it into the centre with the mouth. The tube is dried in the water-oven, and afterwards bent for connection as shown. Its use will be explained later.

All the bulbs are connected in their various places.

Filling the Pipettes.—Before introducing the gas, the liquid in each bulb must be drawn to the height of the taps, or marks on the branches. This is done by raising the bottle, B, previously filled with water, and opening the tap, K. When the water has filled the burette, K is closed and the tap of D is opened. On lowering the bottle, the water runs back out of the burette, and draws over the air in D, the liquid (caustic potash solution) rising and taking its place. As soon as it reaches the mark, the tap is turned off. This procedure is repeated with all the bulbs in succession. With D, the water only rises to the connection with the palladium tube.

The filling of the pipettes may also be more readily accomplished by the rubber-bulb aspirator shown.

Introducing the Gas.—The burette is again filled with water by opening K, and raising the bottle. K is then turned so as to establish connection through the U-tube. The leading tube from the gas sample-bottle is attached to the U-tube, and by lowering the bottle, B, a quantity of the gas is drawn into the burette, water entering the sample-bottle and displacing it. This, however, is not pure. It is mixed with the air in the U and capillary tubes of the apparatus. The gas first drawn in is ejected by turning tap, K, so as to open orifice, L, and by raising the bottle, expelled from the burette. This may be repeated once. If an aspirator-bulb is attached, the air in U-tube and connection may be displaced by its means. When all air is expelled, and only the gas is in the apparatus, the burette is filled by proceeding as before.

Measuring the Gas.—Care must be taken in measuring the gas to hold the levelling bottle, B, so that the level of the water in the burette is exactly the same as in the bottle. 100 c.c. of gas having been drawn over, the tap, K, is turned off, care being taken not to turn it too far. The tap of D is opened, and, by raising the levelling bottle, the gas is passed over into the first bulb. As soon as the water reaches the top of the burette, the tap is turned off, and the gas left in D for a few minutes. The bottle, B, is then lowered, and by opening the tap, the gas is brought back into A, and its volume, after careful levelling, observed. In bringing the gas back for measurement, the absorbing liquid must not pass the mark. After reading off the volume, the gas is again passed into D, brought back, and again measured as before. If no further decrease has taken place, the absorption is assumed to be complete, and the volume is noted. The diminution is the CO_2 absorbed, and reads percentage of volume since 100 c.c. were used.

The same procedure is followed with the second bulb for the absorption of the free oxygen, and with the third for the absorption of CO respectively.

The unabsorbed residue consists of N, H, CH₄. The latter is disregarded, unless specially required. The N and H are estimated thus: The lamp, J, is lit, and the tube containing the paladiumized asbestos warmed carefully. The volume of the residual gas in A having been read off, the bottle, B, is lowered, and tap, K, opened to admit air to 100 c.c. It is then turned off, and, after raising the bottle, tap D, opened, and the mixture of residual gas and air passes into D, over the somewhat heated palladium. This is repeated three or four times, and then the gas brought back for measurement. It is then passed into the potash bulb, D, to remove any CO₂ that may be produced from slight oxidation of the CH₄, and, after bringing into the burette, the volume noted.

Two-thirds of the diminution in volume of the gas and air mixture represents H, the other third is the O taken from the air. That amount (two-thirds) deducted from the original residue leaves the N, and the bulk, almost the whole, of the CH₄.

The statement reads thus—

Original volume of gas	100	c.c.	
After removal of CO ₂	86.5	"	13.5 CO ₂
" " O	86.4	"	0.1 O
" " CO	59.2	"	27.2 CO
Volume of residue N + H	59.2	"	
After admitting air	100	"	
" " passing over Pd	89.7	"	
H and O combined	10.3	"	

$$10.3 \times \frac{3}{2} = H = 6.8 \text{ H}$$

$$59.2 - 6.8 = N = 52.4 \text{ N}$$

There are many other ways of analyzing gases in burettes of various forms and efficiency, and by explosion. For these special treatises on gas analysis must be consulted.

Where SO₂ has to be estimated, it may be effected by the introduction of an extra bulb *before* that used for absorbing CO₂. This bulb is charged with a solution of iodine in potassium iodide, which converts the SO₂ into sulphuric acid.

APPENDIX A.

APPARATUS FOR DRY ASSAY OF MATERIALS FOR TAKING ABROAD.

Steel anvil (small).
 2 toothbrushes.
 Cold chisel.
 1 hammer, with pointed steel ends.
 „ with rounded ends.
 Pliers.
 Cutting-pliers.
 Shears.
 Vice.
 Strong forceps.
 Tongs.
 Crucibles, 1 doz. No. 8; Morgan's salamander, and $\frac{1}{2}$ doz. covers for same.
 6 doz. No. 6 fluxing pots (Morgan).
 4 doz. No. 5 London round; 2 doz. covers for ditto.
 2 doz. Battersea, A; $\frac{1}{2}$ doz. covers.
 4 doz. Battersea, D; 1 doz. covers.
 2 doz. nests copper assay (Juleff's).
 3 doz. gold annealing cups, $1\frac{1}{4}$ -inch.
 1 doz. Berlin porcelain crucibles, No. 1, and covers.
 1 doz. roasting dishes, 3-inch.
 12 doz. scorifiers, $2\frac{1}{4}$ -inch.
 12 doz. cupels, $1\frac{1}{2}$ -inch.
 Cupel mould.
 Mallet.
 Cupel tray.
 Flattening mill.
 Button mould, 2 holes.
 Ingot mould, $6'' \times 2'' \times 1\frac{3}{8}''$.
 Conical mould.
 Copper scoop, 8-inch.
 Wood tray for prills.
 Iron mortar and pestle.

Wedgwood and agate mortars and pestles.
 Tongs, poker, and other furnace tools.

Balances and Weights.

Oertling's assay balance.
 Chemical balance.
 Hand scales and rough balance.
 1 set accurate grm. weights, 100 grms. to 1 mgr.
 1 set rough weights, 100 grms. to 1 mgr.
 1 set pound weights.
 1 set, 50 grms. to 1 kgm. (iron).
 1 set grm. assay weights.

Apparatus.

Porcelain basins, 6 No. 2; 3 each, No. 5, 6, 7.
 Enamelled iron basins, 6 7-inch.
 Beakers, 3 nests, 1 to 8.
 Flasks, Bohemian, 1 doz. each 8, 12, and 20 oz.
 „ „ $\frac{1}{2}$ doz. 40 oz.
 „ Conical, 1 doz. each 10 and 20 oz.
 „ Parting, 1 doz. 1 oz.; 1 doz. 2 oz.; 1 doz. 8 oz.
 Blowpipe.
 12 charcoal blocks.
 Bottles, 1 doz. 12 oz. N.M.
 „ 1 doz. 12 oz. W.M.
 „ 2 doz. 4 oz. N.M.
 4 acid bottles with enamelled labels.
 Corks, 1 gross assorted.

Cork-borers, 1 set.	Test-tube stand.
Covers for beakers, 1 doz. various.	Thermometers.
Pencils to write on glass, 2.	White glazed tile.
Files, 2 triangular; 2 round.	Crucible tongs.
Filter paper, 2 packets each, $5\frac{1}{2}$ -inch and $7\frac{1}{2}$ -inch.	Platinum wire and foil.
" " 1 quire.	Pipeclay triangles.
" stand, 2 holes.	Indiarubber tubing, $\frac{1}{8}$ and $\frac{1}{4}$ inch.
Funnels, $\frac{1}{2}$ doz. $2\frac{1}{4}$ -inch.	1 doz. watch-glasses.
" $\frac{1}{2}$ doz. $3\frac{1}{2}$ -inch.	1 pair weighing-scoops (horn).
" 1 doz. 1-inch, as covers for flasks.	Charcoal combustion furnace.
Sheet-iron portable assay furnace.	4 lbs. good combustion tubing.
Chimney and fittings, with 1 doz. extra muffles.	Charcoal tongs.
Spirit-lamps, or other burners.	
Glass rod, 1 lb.	<i>Materials.</i>
Glass tubing, assorted, 4 lbs.	Hydrochloric acid, 10 Winchesters.
Lens.	Nitric " 6 "
Microscope.	Sulphuric " 2 "
Glazed paper.	Ammonia " 12 "
Mercury bucket.	Bone ash, $\frac{1}{4}$ cwt., No. 1.
Cast iron retort (for mercury) and condenser.	" " $\frac{1}{2}$ cwt., No. 2.
2 sand-baths.	Borax, calcined, $\frac{1}{4}$ cwt.
Scissors.	Charcoal powder, 7 lbs.
Sieves, in nest, 30, 60, 80 mesh.	Sodium carbonate (dry), $\frac{1}{2}$ cwt.
Horn and steel spatulas.	Potassium cyanide, $\frac{1}{2}$ cwt.
2 8-inch iron tripod stands.	" nitrate, $\frac{1}{4}$ cwt.
2 3-ring retort stands.	" chlorate, 10 lbs.
2 clamps for ditto.	Sulphur, 5 lbs.
6 doz. test-tubes, $6'' \times \frac{3}{4}''$ or $5'' \times \frac{5}{8}''$.	Iron nails, 3-inch, 10 lbs.
6 doz. do. $3'' \times \frac{1}{2}''$	Red lead, 1 cwt.
3 test-tube brushes.	Litharge, 1 cwt.
	White argol, $\frac{1}{4}$ cwt.
	Methylated spirit, 2 gallons or more.
	Mercury, 20 lbs., or more.
	Salt.

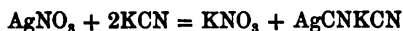
These quantities and materials are sufficient for gold and silver and most of other assays such as are made in a mining camp.

A blowpipe cabinet should be included in every prospector's kit.

APPENDIX B.

THE ASSAY OF POTASSIUM CYANIDE, AND MILL SOLUTIONS CONTAINING CYANIDES, AND METHODS FOR TESTING ORES FOR CYANIDE CONSUMPTION AND SUITABILITY FOR CYANIDE TREATMENT.

Assay of Potassium Cyanide.—The determination of alkaline cyanide (NaCN for metallurgical purposes is estimated and stated as KCN) is based on the fact that silver cyanide is insoluble in solutions of fixed alkalies, or in solutions containing only hydrocyanic acid, but dissolves in ammonia, and in excess of potassium cyanide, forming with it the double cyanide AgCN, KCN . If, therefore, a solution of silver nitrate be added slowly to a solution containing potassium cyanide, the silver cyanide produced by the first additions is at once dissolved in the excess of potassium cyanide in the solution, and the solution of the precipitate will continue till sufficient silver has been added to satisfy the equation given below—



If more silver nitrate be added, it will at once give a turbidity which does not disappear on shaking—



The precipitate consists of silver cyanide, for which no solvent now exists in the solution, all the potassium cyanide having been decomposed or combined.

Standard Silver Nitrate Solution.—Seventeen grms. of pure recrystallized silver nitrate is dissolved and made up to a litre with distilled water free from chlorides and organic matter, and stored away from the light. A considerable quantity of the solution may be made, and its silver contents determined with accuracy by gravimetric and other methods. See Silver.

Since 169.55 grms. of silver nitrate or 107.66 of silver are equivalent to 130 of potassium cyanide, the cyanide value of the solution can easily be calculated when its silver contents are known. There is no satisfactory method of direct standardizing.

The Assay.—If the quality of cyanide is being tested, 10 grms. of the cyanide is weighed out, dissolved in water, and made up to a litre. If the strength of a works solution is being determined, it is used direct. Ten c.c. of the solution is measured out into a flask from a burette (the poisonous nature of cyanide precludes the use of pipettes for this purpose) and about 50 c.c. of water added. The standard silver nitrate solution is then carefully added from a burette till a slight permanent precipitate is formed. The precipitate formed

by the first additions dissolves quickly on shaking, but as the cyanide combines with the silver, only more and more slowly. When near the end the solution should be added drop by drop.

From the consumption of silver nitrate the cyanide present may be calculated by multiplying the silver consumed by—

$$\frac{2\text{KCN}}{\text{Ag}} = \frac{130.04}{107.66} = 1.2078$$

or the silver nitrate by—

$$\frac{2\text{KCN}}{\text{AgNO}_3} = 0.7669$$

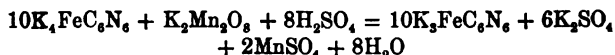
Since silver cyanide only forms soluble double cyanides with alkaline salts; as soon as these are combined according to the reaction given above, any further addition of the silver solution produces turbidity.

Estimation of Free Hydrocyanic Acid.—Free hydrocyanic acid is determined by taking 10 c.c. of the solution and adding excess (about 10 c.c.) of a solution of potassium bicarbonate (KHCO_3) containing 15 grms. of the salt per litre. The solution is diluted, as above, and titrated with the standard silver nitrate. The difference in the silver nitrate consumed in the two experiments is due to free acid. This multiplied by 0.315 gives the free acid. If the strength of the solution is given in silver, then the increase $\times 0.5$ gives the free acid, since $\text{AgNO}_3 = 2\text{HCN}$.

Estimation of Total Cyanides in Solution.—Potassium cyanide, hydrocyanic acid, and the double cyanide of zinc and potassium.

Ten c.c. of the solution is taken, and excess of caustic soda added (about 10 c.c. of a normal solution containing 40 grms. of NaHO per litre). This is diluted, and a few drops of a solution of potassium iodide added. This serves as an indicator. Its strength is immaterial. The titration with silver is continued till a faint yellow opalescence is distinctly seen. The results are expressed in terms of potassium cyanide. If the potassium cyanide and free hydrocyanic acid have been previously determined, the difference will be the cyanide existing in the form of the zinc salt.

Determination of Potassium Ferrocyanide and Sulphocyanate in Solutions.—This is effected by means of a standard solution of potassium permanganate. With ferrocyanide the reaction is as follows:—



The solution of permanganate is made by dissolving 0.5 gm. of the salt in water, and diluting to a litre.

Fifty or 100 c.c. of the solution to be examined is taken and acidified somewhat strongly with sulphuric acid, and cautiously titrated with permanganate till the characteristic pink tint results. This gives total ferrocyanide and sulphocyanate. After determining the sulphocyanate it is deducted, and the remainder gives the ferrocyanide (see below).

Estimation of Sulphocyanides in mill solutions. This is also

accomplished by titration with the permanganate solution given above, the reaction being as follows:—



Fifty or 100 c.c. of the solution is acidified with sulphuric acid, and a slight excess of a solution of ferric chloride or iron alum added, filtered, and washed; or the solution after precipitation may be made to definite bulk, say 200 c.c., and a measured (100 c.c.) portion filtered off. This obviates washing. The filtrate is titrated, and the result calculated to sulphocyanide by multiplying the permanganate consumed by 0.5116.

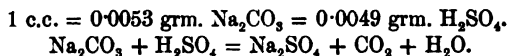
For the ferrocyanide, the permanganate consumed by the sulphocyanide is deducted from the total consumption without the addition of the iron salt, and the difference multiplied by 11.645 gives the ferrocyanide.

Testing Solutions for Soluble Sulphides.—The presence of soluble sulphides may be detected, and their removal effected by shaking with lead carbonate in suspension. If present, the lead carbonate is blackened. If found, they must be removed prior to titration with potassium permanganate.

Determination of the Gold and Silver in Solutions.—A measured quantity of the solution is placed in a lead tray, made by folding up a sheet of pure lead foil 4" × 3" into a tray, 3" × 2" and $\frac{1}{2}$ " deep. The solution is cautiously evaporated to dryness, and the lead and its contents wrapped up and dropped into a hot cupel, and the assay carried out in the usual manner.

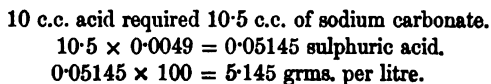
Standard Solution of Acid and Alkali.—

1. **Decinormal Sodium Carbonate.**—5.3 grms. of pure dry sodium carbonate is weighed out, dissolved in water, and made up to a litre—



This salt being procurable in a pure state, and not absorbing water while being weighed, a solution of definite strength can be obtained without difficulty, and by its means the strengths of the others determined accurately.

2. **Decinormal Sulphuric Acid.**—Six c.c. of the concentrated acid are diluted to 2 litres with water. This acid will be more than decinormal, but as sulphuric acid varies in strength, the preparation of an exact solution by a direct method is practically impossible. To make it decinormal, 10 c.c. of the diluted acid is measured by means of a pipette into a beaker, a few drops of a solution of methyl orange added, and titrated with decinormal sodium carbonate till the pink colour is just discharged. Several determinations are made. Since 1 c.c. of the sodium carbonate solution = 0.0049 sulphuric acid (see equation), the quantity of sodium carbonate solution used × by 0.0049 = the sulphuric acid in 10 c.c., and this × 100 = acid per litre. From this the amount of water to be added to make it decinormal may be calculated, e.g.—



Since decinormal acid contains 4.9 grms. per litre.

$\frac{5.145}{4.9} \times 1000 = 1050$ c.c., the volume the solution should occupy, and 50 c.c. of water per litre must be added to make the solution decinormal.

Or calculate thus: Since 1 c.c. $\frac{N}{10}$ $H_2SO_4 = 1$ c.c. $\frac{N}{10}$ Na_2CO_3 , 10 c.c. of the dilute acid contain the quantity that should be present in 10.5 c.c., and the solution must be diluted in the proportion of 10 : 10.5, i.e. $\frac{1}{10.5}$ th of its volume of water added. $\frac{10.5}{10} \times 1000 = 1050 = 50$ c.c. per litre.

In adding water allowance must be made for the amount used from the stock of the solution in determining its strength.

The Decinormal Caustic Soda may then be made by dissolving 5 grms. of caustic soda in water, diluting to a litre, and determining its strength with the standard acid, adding a few drops of methyl orange as an indicator. Water is added to reduce the strength of the caustic soda solution, so that 1 c.c. of the solution is equivalent to 1 c.c. acid; e.g. if on titrating 20 c.c. of the solution with the acid 24 c.c. of acid are required—

20 c.c. = 24×0.0049 sulphuric acid = 0.1176, and 1 litre of the solution = $0.1176 \times 50 = 5.88$ grms. H_2SO_4 .

Since 1 litre should represent 4.9 grms. H_2SO_4 , water must be added in the proportion of—

$$\left(\frac{5.88}{4.9} \times 1000 \right) - 1000 = 1200 - 1000 = 200 \text{ c.c. per litre.}$$

$$\text{Or } 20 : 24 :: 1000 = 1200 - 1000 = 200 \text{ c.c.}$$

Testing Tailings for Acidity.*—

1. **Soluble Acidity.**—Ten grams of the tailings are shaken up with 50 c.c. of water for 10 minutes, and filtered. The filtrate is tested with blue litmus paper. If acid, the residue is washed till washings are no longer acid, and the filtrate and washings titrated with decinormal caustic soda, using a drop or two of methyl orange as an indicator.

2. **Latent Acidity.**—The washed tailings from (1) are washed into a beaker, and a measured quantity, say 22 c.c., of decinormal caustic soda solution added. The whole is well shaken, and the excess of caustic soda solution estimated by titration with decinormal sulphuric acid, using methyl orange as an indicator.

3. **Total Acidity** may be determined directly by shaking up 20 grms. of the tailings with excess of decinormal caustic soda, filtering and determining the excess by titrating the filtrate with decinormal sulphuric acid.

If the tailings are only slightly acid there is no need to do more than determine the total acidity. In the subsequent tests and the actual extraction process the acidity is neutralized by the addition of lime or caustic soda.

Testing Consumption of Cyanide.—Twenty grms. of the ore or tailings are placed in a flask, and, if necessary, sufficient caustic soda added to neutralize any free acid. A measured quantity—50 c.c.—of a potassium cyanide solution of known strength—say 1 per cent.—is then added and allowed to stand, with occasional shaking. It is afterwards filtered and washed, and the excess of cyanide

* H. Van F. Furneaux, A.I.M.E., xxvi. p. 721.

estimated by titration with silver nitrate, with or without the addition of potassium iodide (see above). The difference between the cyanide added and that found is the amount consumed; this is calculated and reported in lbs. per ton (2000 lbs.). Instead of gramme weights, assay ton weights may be employed and the calculation shortened.

Beside the cyanide which is used in dissolving the gold, etc., some ores consume more cyanide on long standing. This will be observed in making the following tests, which are proceeded with if the cyanide consumed in above experiment is not too high. It should not, for ordinary tailings, exceed 4 lbs. per ton.

Laboratory Tests for extraction of gold and consumption of cyanide. Four quantities of 2 assay tons (see p. 34) of the tailings are weighed out, and each placed in a dry 8-oz. bottle, wide-mouthed by preference, and numbered.

1. 10 c.c. of 1 per cent. solution of potassium cyanide and 90 of water are added = 0.1 per cent. KCN.
2. 30 c.c. of the cyanide and 70 of water = 0.3 per cent. KCN.
3. 50 " " " 50 " = 0.5 " KCN.
4. 75 " " " 25 " = 0.75 " KCN.

Whatever quantities of ore or cyanide solution are used in the trials they should not more than half fill the bottles employed. The contents are well shaken and allowed to stand, with occasional agitation, for 48 hours, or if rapid extraction is desired, on an agitator for say 24 hours. It is important that air should have access to the solution, and the stoppers may be left partially off while standing to allow this. The solutions are next filtered through dry filters. Twenty-five c.c. of the filtrate is measured from each and tested for cyanide consumption. Fifty c.c., = 1 assay ton, is examined for precious metal by evaporation in a lead tray (see p. 401). The residues are washed, dried, assayed by the crucible method, and the yield compared with the original ore contents.

$$\frac{\text{Wt. of gold from solution}}{\text{Wt. in ore}} \times 100 = \text{per cent. of extraction;}$$

or, if the ore is not previously assayed—

$$\frac{\text{Wt. of gold from solution}}{\text{Wt. from solution + wt. from tailings}} \times 100 = \text{per cent. of extraction.}$$

The assay of the tailings, after cyaniding, is a most important determination.

Each of the tests is similarly dealt with, and a further test made with the lowest strength of solution which gives best results, on a larger quantity of material weighing from 20 to 100 lbs. or more, using a small vat with a perforated false bottom.

$$\text{Per cent. of extraction} = \frac{B}{A.C} 6.43016$$

when B = wt. of gold extracted in mgrms. A = troy ounces of gold per ton.
C = lbs. of ore taken.

Percolation Test.—One thousand grms. of the ore or pulp are placed in a percolating jar or funnel and neutralized, 250 c.c. of cyanide solution added, and, if necessary, water till the ore is just wetted to the surface. After standing

12 hours, the plug is withdrawn, and solution allowed to percolate for 30 or 50 hours by pouring it back repeatedly on to the pulp. The pulp is drained and the liquor transferred to a measuring flask, the residue being washed with water and the washings added to the original extract.

This is made up to known volume and tested for loss of cyanide and percentage of extraction as above. Many materials give results by percolation which are unobtainable by other means. Ores likely to oxidize give a higher cyanide consumption. If this occurs, the effect of a little free alkali—caustic soda—in the solution should be studied.

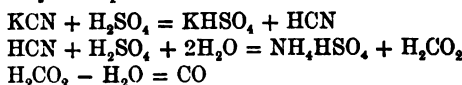
The causes of loss of cyanide are mainly as follows:—

1. $\text{FeSO}_4 + 6\text{KCN} = \text{K}_4\text{FeC}_6\text{N}_6 + \text{K}_2\text{SO}_4$
Consumption for $\text{FeSO}_4 = 2 : 5$ approx.
Fe 1 : 7 ..
2. $\text{ZnSO}_4 + 4\text{KCN} = 2\text{KCNZn}(\text{CN})_2 + \text{K}_2\text{SO}_4$ { ZnSO₄ 8 : 13 ..
Zn 1 : 4 ..
3. $2\text{CuSO}_4 + 6\text{KCN} = 2\text{KCN,Cu}_2(\text{CN})_2^* + 2\text{K}_2\text{SO}_4 + 2\text{CN}$ Cu 1 : 6 ..
4. $\text{Al}_2(\text{SO}_4)_3 + 6\text{KCN} + 6\text{H}_2\text{O} = \text{Al}_2(\text{HO})_6 + 3\text{K}_2\text{SO}_4$
+ 6HCN Al 1 : 7 ..
5. $\text{MgSO}_4 + 2\text{KCN} + 2\text{H}_2\text{O} = \text{Mg}(\text{HO})_2 + \text{K}_2\text{SO}_4 + 2\text{HCN}$ 1 : 7 ..
6. $4\text{KCN} + \text{ZnS} = 2\text{KCN,Zn}(\text{CN})_2 + \text{K}_2\text{S}$ } Zn 1 : 5 ..
 $\text{K}_2\text{S} + \text{KCN} + \text{H}_2\text{O} + \text{O} = 2\text{KHO} + \text{KCNS}$ }
7. $\text{Sb}_2\text{S}_3 + 12\text{KCN} = 2(3\text{KCN,Sb}(\text{CN})_3) + 3\text{K}_2\text{S}$ } Sb 1 : 5 ..
 $6\text{K}_2\text{S} + 6\text{KCN} + 6\text{H}_2\text{O} + 6\text{O} = 12\text{KHO} + 6\text{KCNS}$ }

The sulphates are removable by washing, and the effects of at least the sulphate of alumina and magnesia destroyed by alkaline treatment. The sulphides are not removed by washing, and are the most formidable impurities met with.

Determination of Silver in Cyanide Solutions.—This is based on the decomposition of potassium cyanide, which results on evaporation with sulphuric acid, thus allowing the silver to be precipitated as silver chloride in the ordinary manner.

The reaction may be expressed thus—



Or—



A measured volume of the solution is taken and evaporated nearly to dryness. Strong sulphuric acid is then added in excess, the amount depending on the strength and volume of the solution, and evaporated to complete dryness, or till fumes of sulphuric acid are freely evolved.

After cooling, the residue is carefully taken up with water and, if necessary, heated. There should be no insoluble residue to filter. Hydrochloric acid is then added in excess, and the precipitated chloride filtered off and dealt with as directed (see p. 307).

* This salt decomposes in water and produces $\text{Cu}_2(\text{CN})_2, 6\text{KCN}$. Thus, $3(\text{Cu}_2(\text{CN})_2, 2\text{KCN}) = \text{Cu}_4(\text{CN})_4, 6\text{KCN} + 2\text{Cu}_2(\text{CN})_2$.

The evaporation with sulphuric acid should be conducted under a hood, and if the quantity required is uncertain, it may be added, as required, towards the end of the evaporation till decomposition is complete.

Locating Causes of Non-Extraction by Cyanide.—The causes of non-extraction by cyanide treatment may be: (1) the existence of the gold in too coarse a form for solution; (2) the total destruction of cyanide by reactions given above and by acidity of ore; (3) the combination of the gold with tellurium, bismuth, antimony, and possibly arsenic; (4) the destructive action of soluble sulphides.

The first cause is sought for by amalgamation assay, and points to the necessity, usually followed, of previously amalgamating the ore and treating tailings by cyanide.

Washing with water and weak alkali or the addition of lime is the remedy for the second cause. Ores containing tellurium, etc., may, in some cases, be rendered workable by previous roasting.

Soluble sulphides may be tested for by carbonate of lead.

Ores which contain much kaolin (clay), talc, or other matter yielding fine slimes, if intended for subsequent treatment by cyanide, must be as coarsely crushed as is necessary to remove coarse gold. If fine crushing be necessary, the tailings will be unsuitable for cyaniding, as they will not permit of the ready percolation of the solvent.

APPENDIX C.

TABLES FOR THE SYSTEMATIC QUALITATIVE ANALYSIS OF MINERALS, METALS, ALLOYS, AND SLAGS.

Solution.—If the substance be a mineral or slag it must be reduced to a fine powder by grinding, finally in an agate mortar ; if it be a metal or alloy, drillings, filings, or sawings may be used, but if too hard for drilling or filing it must be reduced to powder in a steel crushing mortar, and if possible the grinding finished in an agate mortar.

The solubility must be determined by heating a very small portion of the powder with dilute hydrochloric acid in a test-tube ; if it is insoluble, another portion should be tested with dilute nitric acid ; and if still insoluble, strong hydrochloric and nitric acids should be tried separately, and afterwards aqua regia if necessary. Should a portion dissolve, it is best to examine the solution obtained apart from that obtained by treatment of the insoluble portion.

If the nature of the body be known, the special means, already recommended under the headings of various metals, may be employed to effect its solution.

Sulphides and arsenides should be roasted to remove the sulphur and arsenic before solution is attempted, and the organic matter should be removed from black band and similar ores in the same manner.

Insoluble bodies and insoluble residues are fused with carbonates of soda and potash, the mass extracted with water, filtered, and the residue treated with acid. The two solutions are examined separately.

If silica be present, excess of hydrochloric acid must be added to the solution in water, which is evaporated to dryness, the residue moistened with hydrochloric acid and again evaporated to dryness. The residue contains the silica, and may contain chlorides of lead, mercury, and silver, for the separation of which see Table I.

The method of solution having been decided on, from 0.5 to 1 grm. of the substance is dissolved for the analysis.

GROUPING TABLE.

Group I. Silver, lead, mercury(ous). The chlorides are insoluble or nearly insoluble in cold dilute hydrochloric acid.

Group II. Lead, bismuth, copper, cadmium, mercury(ic), tin, arsenic, antimony, gold, platinum. The sulphides are insoluble in dilute hydrochloric acid. The group is subdivided into two. The sulphides of arsenic, antimony, tin, gold, and platinum are soluble in yellow ammonium sulphide. The sulphides of the other metals are insoluble.

Group III. Iron, chromium, aluminum (manganese). The hydrates are insoluble in dilute ammonia or ammonium chloride.

Group IV. Nickel, cobalt, zinc, manganese. The sulphides are not precipitated by sulphuretted hydrogen in hydrochloric acid solution, but are insoluble in alkaline solutions.

Group V. Calcium, barium, strontium. The carbonates are insoluble in alkaline solutions.

Group VI. Magnesium, sodium, potassium. The salts of the two last are nearly all soluble, and are examined for separately, after removing the other metals. Magnesium is previously removed by taking advantage of the insolubility of its phosphate in alkaline solutions.

Other less common metals are tested for separately by methods described under the heading of the metal.

TABLE OF GROUP SEPARATIONS.

If not already used, HCl is added to the solution. If any precipitate falls, add HCl to excess. Shake well, and, if warm, cool and filter. Wash precipitate with cold water, and add to filtrate.

PRECIPITATE.

GROUP I.

This may contain Ag, Pb, and Hg. Bi and Sb will be precipitated if present, unless sufficient HCl is added to keep their chlorides in solution.

The precipitate is treated with boiling water and the filtrate tested for lead (p. 58). The residue is treated with ammonia on the paper. A blackening occurs if Hg is present. To the filtrate add HNO_3 till acid. A white precipitate falls = Ag.

PRECIPITATE.

GROUP II.

Warm precipitate with yellow ammonium sulphide for some minutes, filter, and wash. Examine filtrate by B below.

Residue.—Pour hot dilute nitric acid over it on the paper. Any insoluble residue may contain Hg. Dissolve in aqua regia. Evaporate nearly dry, dilute, and add SnCl_2 and heat. A grey precipitate = Hg. Solution may contain Cu, Bi, Cd, Pb. Add a few drops of H_2SO_4 and evaporate nearly to dryness.

PRECIPITATE.

GROUP III.

With possibly phosphates of other metals. Test a small portion of the precipitate by dissolving it in dilute HNO_3 , adding ammonium molybdate, and warming. A yellow precipitate = phosphates. If phosphates be found, dissolve the precipitate in HCl.

Test a drop for iron with $\text{K}_4\text{FeC}_6\text{N}_6$, then neutralize with ammonia, add ferric chloride till yellow and a precipitate for Mn by

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

PRECIPITATE.

GROUP IV.

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

PRECIPITATE.

GROUP V.

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

PRECIPITATE.

GROUP VI.

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

Test by dry tests for Mn, Co, Ni. Wash well. Treat precipitate with cold dilute HCl on paper. Filtrate.—Boil till H_2S is expelled. Add NaOH in excess. Boil and filter. Test precipitate for Mn by

Dilute with water and HCl. Precipitate = Pb as PbSO ₄ . Filter, add to the filtrate ammonia in excess, and filter if necessary. A white precipitate = Bi as BiH ₃ O ₂ . A deep blue coloration = Cu. To this add KCN till the colour disappears, and saturate with H ₂ S. A yellow precipitate = Cd as CdS.	large excess of ammonium acetate. Boil and filter. Add the filtrate to the original filtrate from ammonia. ——— Treatment of precipitate whether before or after separation of phosphoric acid. Dissolve the precipitate in HCl. (a) Test a drop of the solution for iron with K ₂ FeC ₆ N ₆ . A blue precipitate = Fe. (b) To the remainder of the solution add NaHO in excess, boil, and filter. Filtrate.—Make acid with HCl, and add NH ₄ HO in excess, and boil. White precipitate = Al. Confirm by dry test. Residue.—Fuse with KNO ₃ and Na ₂ CO ₃ on Pt. Boil out in water, filter off residue of iron oxide. Add acetic acid to excess, and then lead acetate. Yellow precipitate = Cr.	fusion with Na ₂ CO ₃ and KNO ₃ . Green mass = Mn. To the NaHO solution add one drop of colourless ammonium sulphides. A white precipitate = Zn. Residue insoluble in HCl. Test by borax for cobalt. Dissolve the precipitate in HCl and HNO ₃ . Evaporate till all nitrous fumes are expelled. Carefully neutralize with NaHO. Add KCN in considerable excess, and boil for some time. Then add sodium hypochlorite, solution of bleaching powder, or sodium hypobromide in large excess. A black precipitate = Ni.	Filtrate.—To a small portion add a few drops of CaSO ₄ and stand aside for some time. A white precipitate = Sr. If found, make strongly alkaline with ammonia. Add Am ₂ SO ₄ in large excess, boil, and filter. Precipitate = SrSO ₄ . Filtrate.—Add ammonium oxalate and ammonium hydrate in excess. White precipitate = Ca.	after ignition in a drop of HCl, and test for Na and K by flame. If Mg is absent, K may be identified by adding a few drops of PtCl ₄ and alcohol. A yellow precipitate = K. Mg, if present, is removed before testing for potassium by adding a few crystals of oxalic acid, evaporating to dryness, and heating, taking up with water, and filtering off the MgO. The K and Na pass into the filtrate. This is evaporated to dryness, and tested as above for K.
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The examination for traces and for the rarer metals dealt with in the text must be conducted in the special manner described for such metal.
All results obtained as above must be confirmed by the tests given for each metal.

(see pp. 220 and 254).

APPENDIX D.

LABORATORY BOOK-KEEPING.

IN an assay laboratory next in importance to accurate work is a good system of book-keeping. The results of work done must be recorded in such a way that they can be referred to at once, all details found if required, and calculations, etc., verified.

The actual number of books required will vary with the extent of the work, but, as a rule, they will be at least five. These are—

1. The Sample Book.
2. The Laboratory Index Book.
3. The Rough Bench Book.
4. The Laboratory Book.
5. The Report Book.

The first four books may be of any size, but (except for 3) large post quarto is most convenient.

In addition, a letter book may be advisable, and also in a large laboratory, where work extends over many years, a report ledger, arranged alphabetically as usual under the names of the persons for whom the assays are done.

1. The Sample Book should be ruled as specimen and give the information for the columns provided

No.	Date.	Description and source.	Condition.	Where sampled.	For whom sampled.	By whom sampled.	Weight of bulk.	Weight of sample.	Approximate weight of packets.	Moisture.	No. in Laboratory Index-book.

In cases where the packets are sent out as a basis of purchase, each entry should be followed by the names of the recipients of the packages.

2. The Laboratory Index-Book is of very great importance, as it is the key to the whole system. It should be large post 4to, and should be ruled as in the accompanying example, preferably across two pages.

No.	Re- ceived.	Description.	Mark.	From.	Remarks.	Report sent.	Gr. assay	Gr. assay
	1899							
1037	Nov. 16	Pyritous gold ore	Hetty Green	J. Thomson, Esq.	From British Columbia	Nov. 20	114	256
1058	" "	"	Lily May					
1059	" "	Gold concentrates	B. Q. 2	W. Smith, Esq.	S. Africa. Mine not known	" 21	115	257
1060	" 17	Platiniferous sand	—	L. Jones, Esq.	Gathered in S. Africa; brought home by Mr. Jones for examination	Dec. 16	131	263
1061	" "	White metal	W. W.	Shaw & Co.	Police court case	Nov. 19	113	255

Immediately a sample is received it should be given a number by which it is known in the laboratory. This is entered in the book, with all the necessary particulars. When the work is complete, the date when the report was sent is entered, and also the pages in the Laboratory Book and Report Book where particulars are to be found.

The entries given as a specimen will sufficiently indicate the nature of the entries.

3. **The Rough Bench Book.** This should be 8vo size; in it are entered the results of all weighings, titrations, etc., as they are done. The entries should be made direct, no erasures or tearing out of leaves should be allowed, and under no circumstances should weighings or results, even if only needed temporarily, be entered on scraps of paper. Each page should be devoted to one sample only, and should bear at the top the number of the sample to which it relates, as described in the Laboratory Index-Book. These books should be carefully preserved, and of course if there are several assistants, each will need his own book, and in that case when he has completed the assay, he should summarize it for entry in the Laboratory Book.

4. **Laboratory Book.** This is the book that contains the work done. All results should be entered in such detail that they can be recalculated from the figures. It should not be a mere statement of results. In the case of dry assays the flux mixture used should be specified, etc.

The amount of detail to be given will vary with the taste of the assayer and the variety of the work to be done.

The following forms will indicate the nature of the detail, though it must always be remembered that it is better to give too much information than too little.

SAMPLE PAGES FROM LABORATORY BOOK.

RELATING TO A GRAVIMETRIC ASSAY.

No.
 Sample of:—
 Determination of:—
 Method used:—
 Assayed by:—
 No. of Rough Bench Book:—

Weight of precipitate.	Name of substance precipitated.	Factor used.	Substance determined.	Weight.	Per cent.

Remarks:—

RELATING TO A VOLUMETRIC ANALYSIS.

No.
 Sample of:—
 Determination of:—
 Standard solution used:—

Standardizing:—

Weight of substance used for standardizing.	C.C. of standard solution used.	1 c.c. =
1.		
2.		
3.		

Mean

Assay method used:—
 Assayed by:—
 No. of Bench Book:—

Weight taken.	Cubic centimetres of standard solution used.	Weight found.	Percentage.
1.			
2.			

Remarks:—

IRON ASSAY (CRUCIBLE).

No.

Character of ore:—

Appearance, etc.:—

Assayed by:—

Charges.	1.	2.	3.	4.
Ore				
Silica				
Lime				
Glass				
Kaolin				
Fluorspar				
Time in fire				

Slag, colour:—

„ appearance:—

Button, weight:—

„ character:—

Remarks:—

GOLD AND SILVER CRUCIBLE ASSAY.

No.

Character of ore:—

Assayed by:—

No. of Rough Bench Book:—

DETERMINATION OF REDUCING POWER.

Reducing power.	Grammes of ore employed.	Grammes of lead obtained.	Reducing power per gramme.

Charge.	No. 1.	No. 2.
Ore		
Litharge		
Soda		
Borax		
Argol		
Salt		
Nitre		

In fire to fusion:—

„ after fusion:—

Gold and Silver Crucible Assay (continued).

Slag, colour, etc. :—
 Lead button—
 Weight :—
 Character :—
 Scorification of lead button.
 Fluxes :—
 Weight after first scorification :—
 " second " :—
 Cupellation.
 Bullion obtained :—
 Parting.
 Gold, weight :—
 ozs. per ton :—
 Silver, weight :—
 ozs. per ton :—
 Remarks :—

SCORIFICATION ASSAY OF SILVER AND GOLD.

No.
 Character of ore :—
 Assayed by :—
 No. of Rough Bench Book :—

Charge	1.	2.	3	4.
Ore... 				
Borax 				
Silica 				
Sodium carbonate ...				

Slag.
 Colour, appearance, etc. :—
 Lead button.
 Weight :—
 Character :—
 Weight after second scorification (if necessary) :—
 " third " "

Cupellation :—
 Total bullion :—
 Gold, weight :—
 " ozs. per ton :—
 Silver, weight :—
 Silver in lead (deducted) :—
 Silver in ore :—
 " " ozs. per ton :—
 Remarks :—

GOLD BULLION.

No.
 Description :—
 Assayed by :—
 No. of Rough Bench Book :—
 Base metal assay—
 Bullion, weight employed :—
 Lead, weight employed :—
 Gold and silver found :—
 Base metal (difference) :—
 Inquartation—
 Bullion :—
 Silver added :—
 Lead :—
 Parting—
 Bullion, weight :—
 Gold "
 " ozs. per ton :—
 Remarks :—

SILVER BULLION (DRY ASSAY).

No.
 Assayed by :—
 No. of Rough Bench Book :—
 Description :—
 Cupellation—
 Weight of bullion employed :—
 " lead employed :—
 " silver found :—
 " assay loss (added) :—
 Fineness :—

VOLUMETRIC ASSAY.

Weight of bullion taken :—
 Salt solution, normal, cubic centimetres required :—
 " decinormal " "
 " total " "
 Silver solution—
 Total salt required :—
 Silver equivalent :—
 Fineness :—
 Remarks :—

5. **Report Book.** A report will usually be sent of any work which is done. This should be written in copying ink, and copied into the Report Book, which, therefore, should be an ordinary letter-copying book.

**Laboratory and Assay Office,
10A, Blank Street,
Blanktown,
Blankshire.**

In all correspondence relating to this report, please quote No. .

[illegible]

(Signed)

Sampler.

The following is a convenient way of sending reports :—

Laboratory and Assay Office,
10A, Blank Street,
Blanktown,
Blankshire.

_____ 19__.

In all correspondence relating to this report, please quote No.

Report on a sample of _____ received from Messrs. _____ on the _____ day of _____, 19__.

Marks and description.	No. in Laboratory Index book.	Constituents found, ozs. per ton.	Remarks.

2 E

(Signed) _____
Total _____

In gold and silver assays under the heading of constituents found, per cent., or oz. per ton, either of the lines may be struck out as required when writing the report.

All possible matter should be printed, and the letter book in which they are copied should be provided with a heavily-printed form, which can be placed behind any one of the reports when it is desired to refer to them. The book should be paged and indexed.

Under the heading, "In all correspondence relating to," etc., the page of the report book should be written so that from the information there gained, any part of the assay may be referred to.

6. **Letter Book.** It sometimes happens that letters pass concerning assays which are not reports. These should be copied into the letter book, and if of importance, reference can be made to them in the Remarks column of the Laboratory Book.

7. **The Assay Ledger** will only be necessary in large laboratories. The card index system is very convenient in place of a book.

Sample of Card.

Name _____
Sample of _____
Address to which sent _____
Date _____
Page in Report Book.

These can be kept in alphabetical order in a shallow drawer divided lengthwise by partitions, the cards standing on edge.

APPENDIX E.

METRIC STANDARDS AND ENGLISH EQUIVALENTS.

- 1 metre = 39·37 English inches.
 1 litre = 1 cubic decimetre = 1000 cubic centimetres = 1·7 pint
 1 gramme = weight of 1 cubic centimetre of water @ 4° C. = 15·432 grains

SUNDRY WEIGHTS AND MEASURES.

1 lb. Avoirdupois	=	7000 grains
1 oz. "	=	437½ "
1 lb. Troy	=	5760 "
1 oz. "	=	480 "

NOTE.—The troy and apothecaries' ounce are identical, but chemicals are sold by avoirdupois weight.

1 gallon of water	=	70,000 grains = 10 lbs.
1 pint "	=	20 ozs. or 8750 grains
1 cubic inch of water	=	252·458 grains
1 cubic foot "	=	62½ lbs. = 1000 ozs. = 437,500 grains
1 litre of water	=	15,432 grains
1 oz. "	=	1·73298 cubic inches

MULTIPLIERS TO CONVERT ENGLISH INTO METRIC MEASURES.

	Multiply by
Yards to metres 	0·914379
Gallons to litres 	4·543389
Cubic inches to litres 	0·016386
Grains to grammes 	0·064792
Pounds Avoirdupois to kilogrammes	0·453554

TO CONVERT

Metres to yards 	1·093639
Litres to gallons 	0·220100
Litres to cubic inches 	61·028028
Grammes to grains 	15·432
Kilograms to pounds avoirdupois	2 204857

DECIMAL MULTIPLIERS.

To reduce cubic inches to pints ...	0·028848
" " " gallons ...	0·003606
" " " cubic feet ...	0·0005787
" cubic feet to gallons ...	0·6232

ELEMENTS AND ATOMIC WEIGHTS.

According to the German Chemical Society's standard, 1898, 0 = 16.

Metallic.

Name.	Symbol.	Atomic weight.
Aluminium	Al	27.1
Antimony	Sb	120.0
Arsenic	As	75.0
Barium	Ba	137.4
Beryllium (Glucinum)	Be	9.1
Bismuth	Bi	208.5
Cadmium	Cd	112.0
Caesium	Cs	133.0
Calcium	Ca	40.0
Cerium	Ce	140.0
Chromium	Cr	52.1
Cobalt	Co	59.0
Copper (Cuprum)	Cu	63.6
Didymium	Di	—
Erbium	Er	166.0
Glucinum (Beryllium—Be)	Gl	9.1
Gold (Aurum)	Au	197.2
Indium	In	114.0
Iridium	Ir	193.0
Iron (Ferrum)	Fe	56.0
Lanthanum	La	138.0
Lead (Plumbium)	Pb	206.9
Lithium	Li	7.08
Magnesium	Mg	24.36
Manganese	Mn	55.0
Mercury (Hydrargyrum)	Hg	200.3
Molybdenum	Mo	96.0
Nickel	Ni	58.7
Niobium	Nb	94.0
Osmium	Os	191.0
Palladium	Pd	106.0
Platinum	Pt	194.8
Potassium (Kalium)	K	39.15
Rhodium	Rh	103.0
Rubidium	Rb	85.4
Ruthenium	Ru	101.7
Silver (Argentium)	Ag	107.93
Sodium (Natrium)	Na	23.05
Strontium	Sr	87.6
Tantalum	Ta	183.0
Thallium	Tl	204.1
Thorium	Th	232.0
Tin (Stannum)	Sn	118.5
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	239.5
Vanadium	V	51.2
Yttrium	Y	89.0
Zinc	Zn	65.4
Zirconium	Zr	90.6

TABLE OF FACTORS.

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Non-Metallic.

Name.	Symbol.	Atomic weight.
Argon	A	40.0(?)
Boron	B	11.0
Bromine	Br	79.96
Carbon	C	12.0
Chlorine	Cl	35.45
Fluorine	F	19.0
Hydrogen	H	1.01
Iodine	I	126.85
Nitrogen	N	14.04
Oxygen	O	16.0
Phosphorus	P	31.0
Selenium	Se	79.1
Silicon	Si	28.4
Sulphur	S	32.06
Tellurium	Te	127.0
(?) Helium	He	4.0(?)
(?) Samarium	Sa	150.0(?)

POUILLET'S SCALE OF TEMPERATURE.

	°C.
Incipient red heat	525 (this is a little too low).
Dull red	700
Incipient cherry red	800
Cherry red	900
Full red	1000
Deep orange	1100
Clear "	1200
White, clear yellow	1300
Bright white	1400
Dazzling white	1500-1600

These are only given for approximating the temperatures of furnaces. If measurements are required, either the specific heat or the Austen Chatelier pyrometer must be used. For temperatures below redness, thermometers reading to 500° C. are obtainable.

TABLE OF FACTORS.*

Metal.	Form in which weighed.	Form in which required.	Multiplier for weight of precipitate.
Aluminium	Alumina, Al_2O_3	Metal, Al	0.53279
"	Aluminium phosphate, $Al_2(PO_4)_3$	"	0.2236
Ammonium	Ammonium chloro - platinate, $2NH_4Cl, PtCl_4$	Ammonia, NH_3	0.07865

* Calculated on the atomic weights in general use—
H = 1

Metal.	Form in which weighed.	Form in which required.	Multiplier for weight of precipitation.
Antimony *	Antimony tetroxide, Sb_2O_4	Metal, Sb	0.78988
	" "	Sulphide, Sb_2S_3	1.10598
	" "	Trioxide, Sb_2O_3	0.94878
	Antimony trisulphide, Sb_2S_3	Metal, Sb	0.71441
Arsenic	" "	Sulphide, Sb_2S_3	0.85693
	" "	Trioxide, Sb_2O_3	0.0398
	Arsenio-molybdate	Arsenic, As	0.3949
	Magnesium-ammonium-arsenate, $2(\text{MgNH}_4\text{AsO}_4)\text{H}_2\text{O}$	Arsenic anhydride, As_2O_3	0.60526
	" "	Arsenic trioxide, As_2O_3	0.52112
	Ammonia magnesia arsenate, $(\text{MgNH}_4\text{AsO}_4)\text{H}_2\text{O}$	Metal, As	0.60959
	Arsenious sulphide, As_2S_3	Trioxide, As_2O_3	0.80443
	" "	Metal, As	0.1783
Barium	Lead arsenate	Baryta, BaO	0.65669
Bismuth	Sulphate, BaSO_4	Metal, Bi	0.89767
Bromine	Bismuth trioxide, Bi_2O_3	Bromine, Br	0.42554
Cadmium	Silver bromide, AgBr	Metal, Cd	0.87490
	Cadmium oxide, CdO	" "	0.77727
Calcium	Cadmium sulphide, CdS	Metal, Ca	0.70961
	Calcium oxide, CaO	Lime, CaO	0.55599
Carbon	" carbonate, CaCO_3	Carbon, C	0.27273
	Carbon dioxide, CO_2	Carbon dioxide, CO_2	0.22319
Chlorine	Barium carbonate, BaCaO_3	Chlorine, Cl	0.24729
	Silver chloride, AgCl	Hydrochloric acid, HCl	0.25428
Chromium	Chromic oxide, Cr_2O_3	Metal, Cr	0.68640
	" "	Chromic acid, CrO_3	1.31359
	Lead chromate	Metal, Cr	0.16241
	" "	Chromic acid, CrO_3	0.31081
Cobalt	" "	Chromic oxide, Cr_2O_3	0.23661
	Nitrite, $\text{Co}(\text{NO}_2)_2$	Metal, Co	0.12985
Copper	Sulphate, CoSO_4	" "	0.37948
	Oxide, CuO	Metal	0.79864
	Sulphide, Cu_2S	" "	0.79834
Iodine	" "	Cuprous oxide, Cu_2O	0.89898
	Silver iodide, AgI	Iodine, I	0.54029
Iron	Ferric oxide, Fe_2O_3	Metal, Fe	0.70016
	" "	Ferrous oxide, FeO	0.90007
Lead	Metallic, Pb	Sulphide, PbS	1.15494
	Lead sulphate, PbSO_4	Metal, Pb	0.68295
	" "	Oxide, PbO	0.73576
	Lead oxide, PbO	Metal, Pb	0.92822
Magnesium	Lead chromate, PbCrO_4	" "	0.63972
	Magnesia, MgO	Magnesium carbonate, MgCO_3	2.10000
	" "	Metal, Mg	0.21614
	Magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$	Magnesia, MgO	0.36036
Manganese	Manganese dioxide, MnO_2	Metal, Mn	0.63191
	" "	Manganous oxide, MnO	0.81595
	Trimanganese tetroxide, Mn_3O_4	Metal, Mn	0.72029
	" "	Oxide, MnO	0.93007
Mercury	Metal, Hg	Cinnabar, HgS	1.15859
	Mercuric sulphide, HgS	Mercury, Hg	0.86202

* Sb = 120.

TABLE OF FACTORS

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Metal.	Form in which weighed.	Form in which required.	Multiplier for weight of precipitation.
Molybdenum	Molybdate of lead, PbMoO_4	Molybdenum, Mo	0.26131
Nickel	Nickelous oxide, NiO	Metal, Ni	0.78595
Phosphorus	Pyrophosphate of magnesia, $\text{Mg}_2\text{P}_2\text{O}_7$	Phosphorus, P	0.27953
	" " "	Phosphoric anhydride, P_2O_5	0.63977
	Phosphomolybdate of ammonia	Phosphorus, P	0.01630
	" " "	Phosphoric anhydride, P_2O_5	0.03730
	" " "	Phosphate of lime, $\text{Ca}_3(\text{PO}_4)_2$	0.08142
Potassium	Potassium sulphate, K_2SO_4	Potassium oxide, K_2O	0.54077
	Potassium chloroplatinate, 2KClPtCl_6	Potassium, K	0.16107
	" " "	" oxide, K_2O	0.19399
	" " "	" chloride, KCl	0.30771
Platinum	Ammonium chloroplatinate, $2\text{NH}_4\text{ClPtCl}_6$	Platinum, Pt	0.43926
Silicon	Silica, SiO_2	Silicon, Si	0.46729
Silver	Silver chloride, AgCl	Silver, Ag	0.75271
	" iodide, AgI	"	0.45971
Sodium	Sodium sulphate, Na_2SO_4	Sodium oxide, Na_2O	0.43681
	"	Sodium, Na	0.32426
Strontium	Strontium sulphate, SrSO_4	Strontium, SrO	0.47645
Sulphur	Barium sulphate, BaSO_4	Sulphur, S	0.13748
Tin	Stannic oxide, SnO_2	Tin, Sn	0.78680
	" sulphide, SnS_2	"	0.64817
Titanium	Titanic oxide, TiO_2	Titanium, Ti	0.60060
Tungsten	Tungstic acid, WO_3	Tungsten, W	0.79351
Uranium	Oxide, U_3O_8	Metal, U	0.81938
Vanadium	Ammonium vanadate, Am_2VO_4	Vanadium, V	0.30288
	Vanadic anhydride, V_2O_5	"	0.28101
Zinc	Zinc oxide, ZnO	Zinc, Zn	0.80263
	Zinc sulphide, ZnS	"	0.66990
	" "	Zinc oxide, ZnO	0.83464

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THE END.

A
CLASSIFIED CATALOGUE
OF
SCIENTIFIC WORKS

PUBLISHED BY
MESSRS. LONGMANS, GREEN, & CO.
LONDON: 39 PATERNOSTER ROW, E.C.
NEW YORK: 91 & 93 FIFTH AVENUE.
BOMBAY: 32 HORNBY ROAD.

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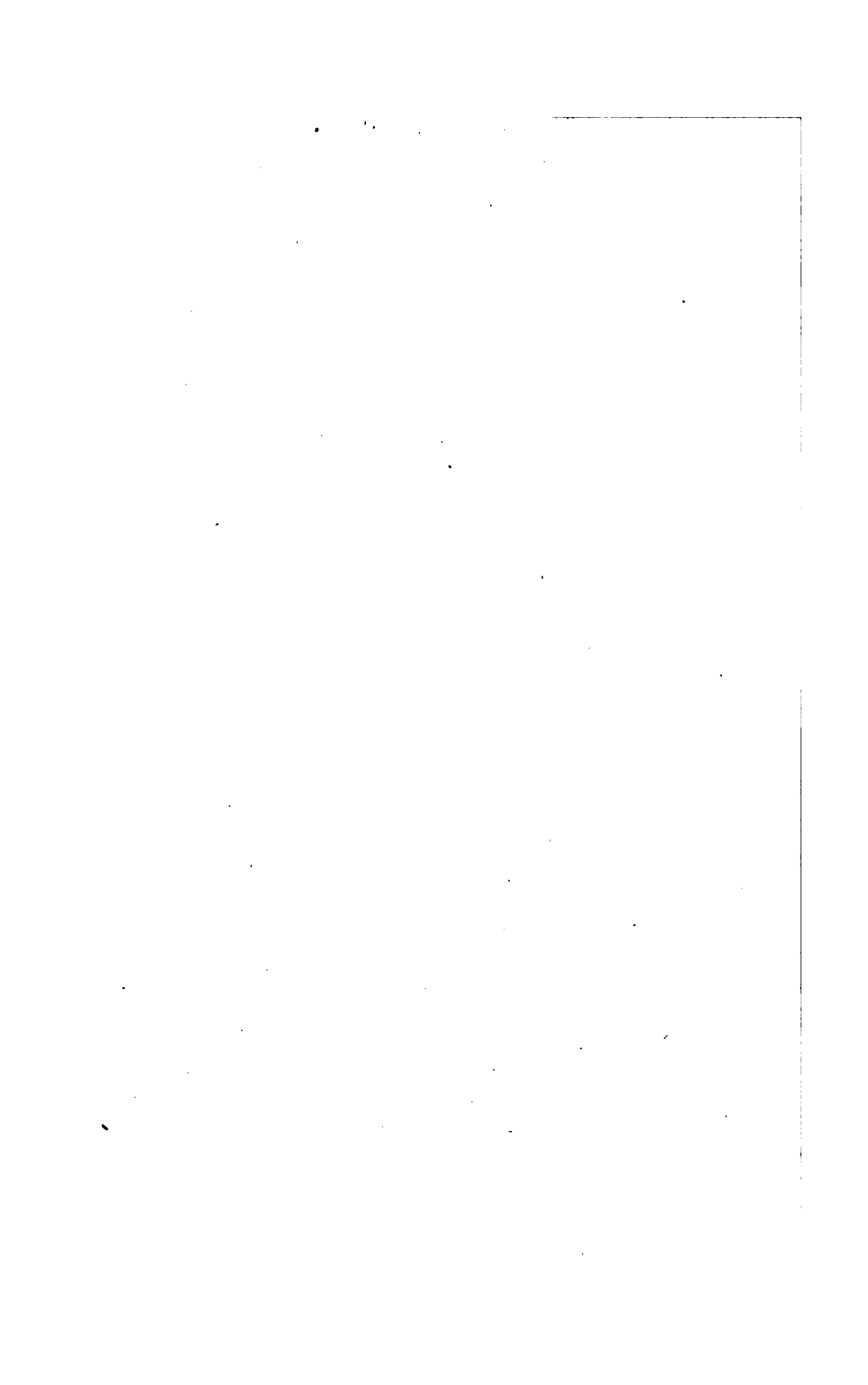
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